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THE DIFFERENTIAL THERMAL ANALYSIS OF CERTAIN CARBONATE MINERALS

A.G. SWAN

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THE DIFFERENTIAL THERMAL ANALYSIS OF CERTAIN CARBONATE MINERALS

with special reference to

THE APPROXIMATE DETERMINATION OF DOLOMITE CONCENTRATIONS

A DISSERTATION

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

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by

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ABSTRACT

A description of a differential thermal analysis apparatus and a detailed procedure for its operation is presented.

The variables inherent in the differential thermal analysis of minerals are investigated. Rate of heating is found to be an important factor in obtaining the maximum data on a thermal curve.

It is shown that the thermoelectric voltage generated during the first stage in the dissociation of a particular dolomite sample remains constant when the specimen weight exceeds a certain value. From the differential thermal analysis of dolomitic limestones and synthetic dolomite-calcite mixtures, the area of the lower-temperature dolomite peak and the concentration of dolomite, calculated from chemical analyses, are shown to be proportional.

Improved thermal curves of cerrusite are contributed, which, due to increased thermal response and reduced rate of heating, can be interpreted in accordance with the known chemical data.

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I. INTRODUCTION

A. General Statement.

Under the general program of the Research Council of Alberta the Geological Section undertook a study of the fine-grained sediments characteristic of much of the surface and sub-surface deposits of Alberta. As one method of approaching this study it was decided to use differential thermal analysis[1] as the first step toward a more comprehensive investigation that is to include the use of x-ray spectroscopy. The d.t.a. technique has so far received only limited application in Canada but has been widely used both by American and European investigators.

During September and October 1952, the thermal apparatus and electronic recorders were assembled as a complete unit for d.t.a. Enough flexibility in the mechanical and electrical arrangements was retained in order to permit a study of the fundamentals upon which standard procedures have been adopted by other workers.

B. Acknowledgements.

The preparation of this thesis has been under the direction of Dr. D.H. Simpson, Department of Geology, University of Alberta, and of Mr. G.A. Collins, Research Council of Alberta. Thanks are extended to them and to Mr. S.J. Groot for his help in the preparation of the drawings.

[1] Hereinafter referred to as d.t.a.

C. Purpose of the Investigation

After installation of the equipment considerable time was spent in observing its response under varying experimental conditions, in calibration of the temperature scales and in becoming familiar with the procedures already established by other workers. After operating techniques were acquired, three specific problems were investigated:

1. To set up standard thermal curves for known mixtures of dolomite and calcite, and for carbonate rocks of known chemical composition in order to aid in the semi-quantitative analysis of dolomitic limestones.

2. To relate the chemistry of the $PbCO_3$ - PbO system to the published results of d.t.a.

3. To relate the chemistry of the $MgCO_3$ - MgO system to the published results of d.t.a.

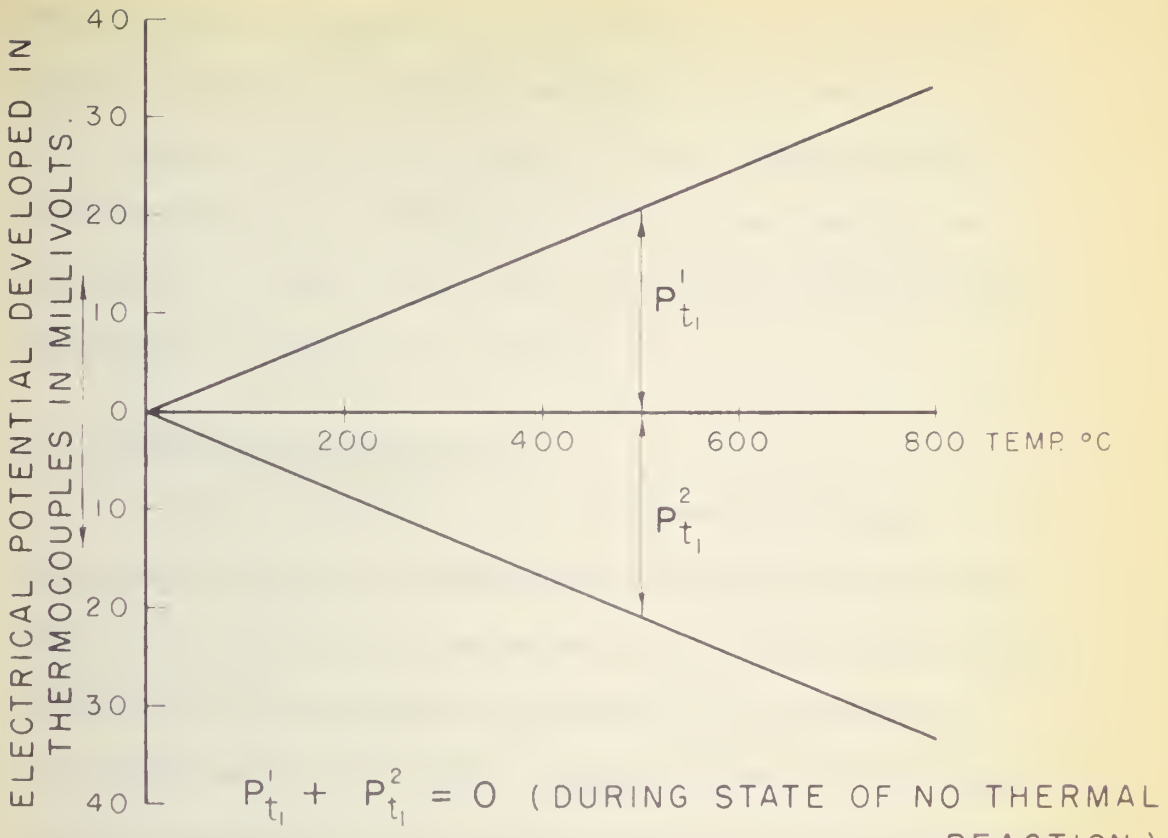
D. Method of Investigation

The differential thermal technique for the analysis of fine-grained sediments was first applied by Le Chatelier in 1887. It has become one of the major techniques in the identification and characterization of clays, but it is applicable also to other minerals. Unlike chemical methods of analysis, it allows rapid identification and semi-quantitative analysis of mineral constituents whether or not the presence of such minerals is suspected.

The basic principle of the d.t.a. method remains unchanged since its inception. It takes into account the fact that a mineral upon the application of heat may undergo reactions such as loss of adsorbed and crystalline water, oxidation, crystal inversion and decomposition, all accompanied by either evolution or absorption of heat. Thus, if both a reactive mineral and an inert substance are heated together at constant rate, temperature differences will be set up between them when a thermal reaction takes place in the mineral.

These temperature differences are determined by use of a dual-terminal thermocouple, one head of which is placed in the sample while the other is placed in the inert material. The connections are so arranged that the electrical potentials developed in the thermocouples during heating are opposed and hence when there is no reaction in the sample the potentials balance (Figure 1). Any heat effect in the sample upsets this balance and the resultant potential difference is traced by a recording potentiometer as a peak on a continuously moving chart.

On heating calcite an intense endothermic reaction, corresponding to the decomposition of the $CaCO_3$ molecule and the liberation of CO_2 as a gas phase, takes place approximately between 700°C and 860°C. A sample of powdered quartz, on the other hand, exhibits only a sharp endothermic reaction at about 573°C corresponding to the inversion of its crystal structure from the trigonal to the hexagonal form. A mixture of calcite and quartz, such as might occur naturally in a mineral aggregate, will therefore show



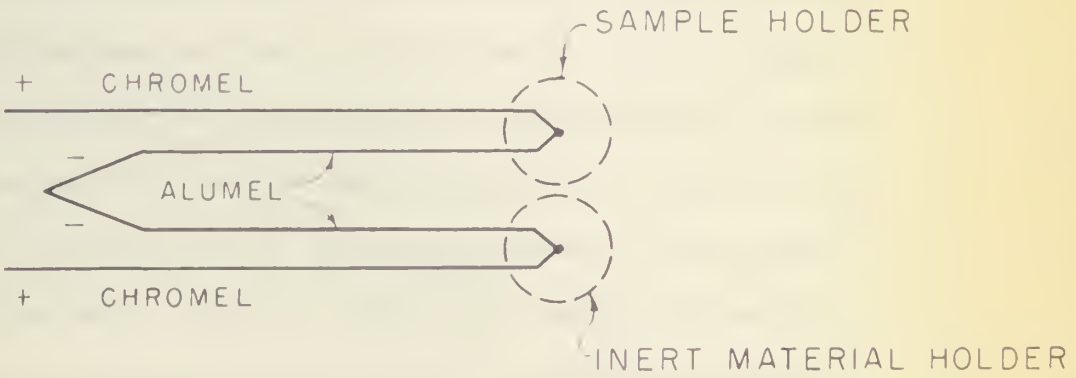


FIGURE I. ARRANGEMENT OF DIFFERENTIAL THERMOCOUPLES TO ACHIEVE BALANCE OF POTENTIAL.

two endothermic reactions as it is heated in the differential thermal apparatus through the temperature range mentioned above. The potential differences arising from the thermal effects of these reactions will therefore be shown on the chart as two deflections or peaks on one side of a straight base-line which represents the state of no reaction.

E. Theoretical Considerations.

As a thermal curve is a differential function, measuring differences in temperature between the specimen and the inert standard, it is dependent only on those effects which do not occur simultaneously and equally in the substances surrounding each thermocouple. Absolute symmetry of spacing of the thermocouples, the specimen holes and the specimen block relative to the heating coil of the furnace will ensure equal heating of the thermocouples when the sample holes are empty. When the specimen and inert material are in place, however, two other effects must be considered: the differential heat flow from the block to the thermocouple in the centre of each material, and the heat of any thermal reaction taking place in the specimen. The first effect is a small differential temperature arising from differences in thermal conductivity and specific heat of the two materials.

Figure 2 shows the thermal curve for a specimen of magnesite. Below 400°C the heat inflow to both thermocouples

is approximately the same and no major differences in their temperatures are recorded. This gives rise to a comparatively straight base-line with minor displacements probably due only to dehydration and to small temperature differences arising from differences in thermal conductivity and specific heat between the magnesite and the inert standard (alundum). Above 400°C the dissociation of the magnesite is accompanied by absorption of heat from its surroundings and the specimen thermocouple becomes cooler than the inert standard thermocouple. This endothermic effect increases to 660°C at which temperature the rate of absorption equals the rate of differential heat conductivity into the specimen. Thereafter, the endothermic effect begins to decrease more rapidly than the inflow of heat from the furnace. At some unknown temperature between this point and the point at which the base-line is again established, the reaction ceases. The whole reaction is therefore considered to take place between the temperatures marked by the points where the thermal curve deviates from and returns to the base-line.

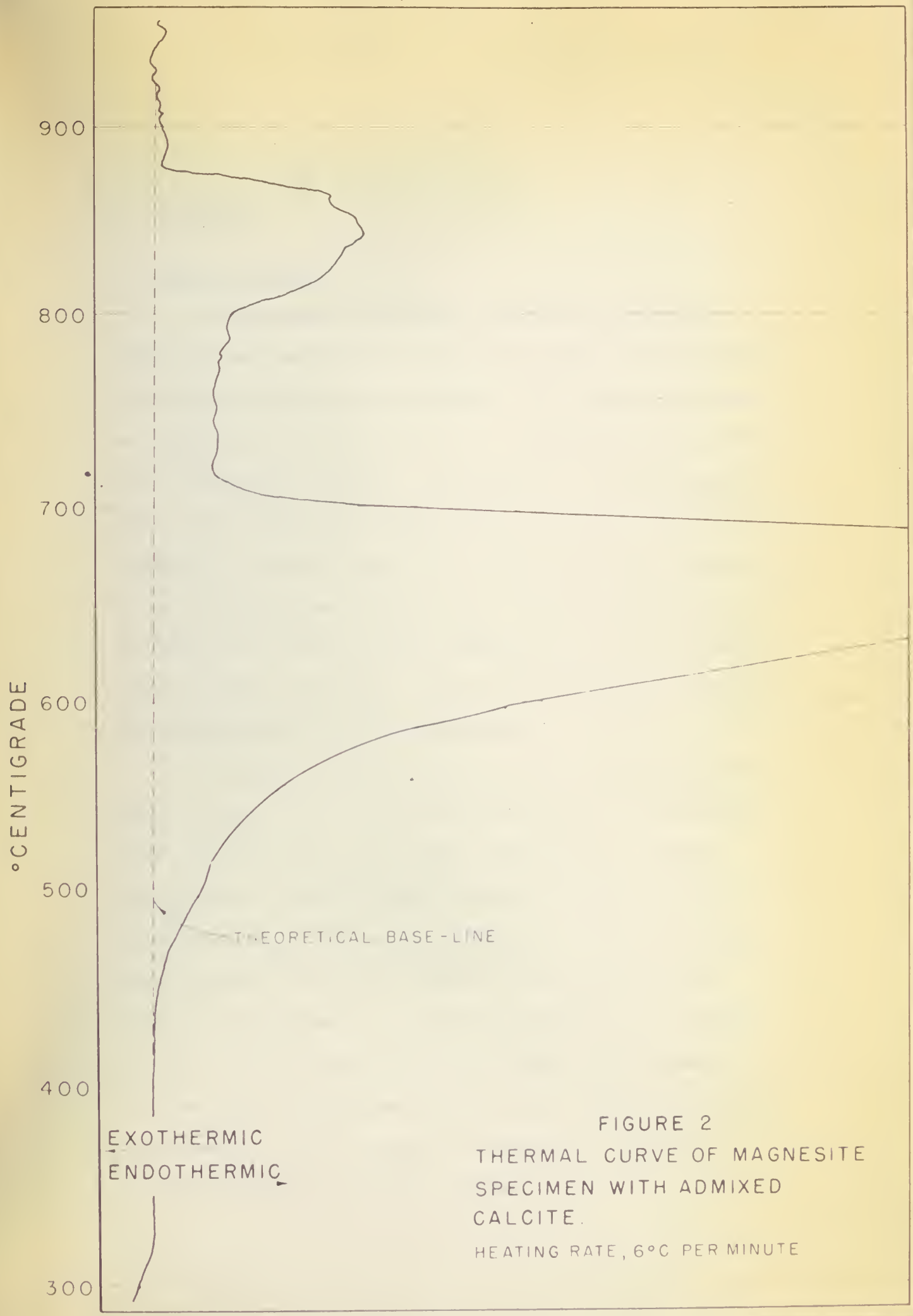


FIGURE 2
THERMAL CURVE OF MAGNESITE SPECIMEN WITH ADMIXED CALCITE.
HEATING RATE, 6°C PER MINUTE

II. APPARATUS

A. General Statement.

The simplest and earliest apparatus for recording thermal curves consisted only of a galvanometer, the deflections of which were recorded by the operator. This tedious operation was supplanted in 1939 by the use of a camera-galvanometer which gave a photographic record of the movements of the galvanometer mirror. Two drawbacks to this refinement were the necessity for operating in a darkened room and the inability of the operator to observe the progress of the record. The later development of the "photopen" recorder and its application to d.t.a. provided a means of making a continuous record of the galvanometer readings and was described in 1948 by R.A.Rowland.

The first departure from the use of the photographic type of recorder came in 1948 when Kerr and Kulp (12) obtained direct thermal curves using a Leeds and Northrop recording potentiometer. This instrument allowed the simultaneous and direct recording of several thermal curves of different samples heated together in the same furnace. In this laboratory an electronic potentiometer is used but at present it is arranged to record only one thermal curve at a time. The arrangement of thermocouples and specimen holder together with the mechanism for controlling rates of heating are based upon information provided by the Bureau of Mines, Ottawa.

The assembled apparatus for differential thermal analysis is shown in Plate 1, and consists of five units:

An electrical furnace and transformer.

A specimen holder and attachments.

A program controller.

A differential temperature recorder.

A furnace temperature recorder.

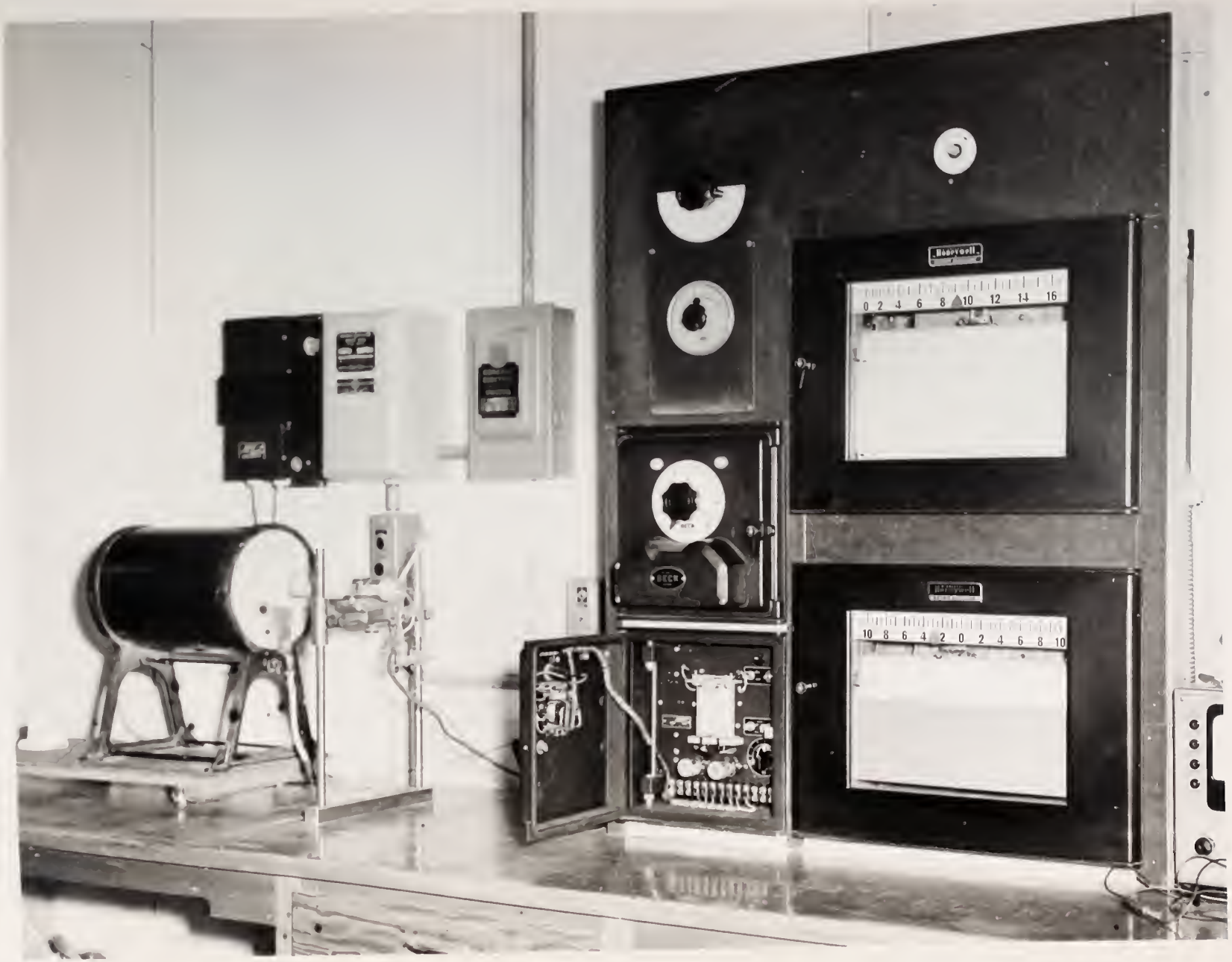
B. Furnace.

The furnace used is a Hoskins 305 electrical resistance furnace with a cylindrical liner of alundum around which a coil of chromel A wire, 1/8 inches in diameter, is wound. This heating element is designed to operate on a 60 cycle, 20 volt, 50 ampere alternating current which is applied intermittently by a relay in the program controller to give the rate of heating desired. Excessive heat loss is prevented by a layer of firebrick 2 inches thick which is packed around the outside of the heating coil, but temperatures above 1150°C cannot be attained.

The furnace is mounted horizontally on a moveable carriage fitted with castor wheels which allow the whole unit to be slid horizontally to enclose the specimen holder before a run is made. It is claimed by Kerr, Kulp and Hamilton (13) that a vertically mounted furnace permits greater symmetry in the placement of the specimen holder within the furnace liner. This arrangement, however, requires the use of an elaborate system of pulleys and counter-weights in order to raise and

PLATE 1.

Differential Thermal Analysis Equipment.


Honeywell
0 2 4 6 8 10 12 14 16
Honeywell
10 8 6 4 2 0 2 4 6 8 10

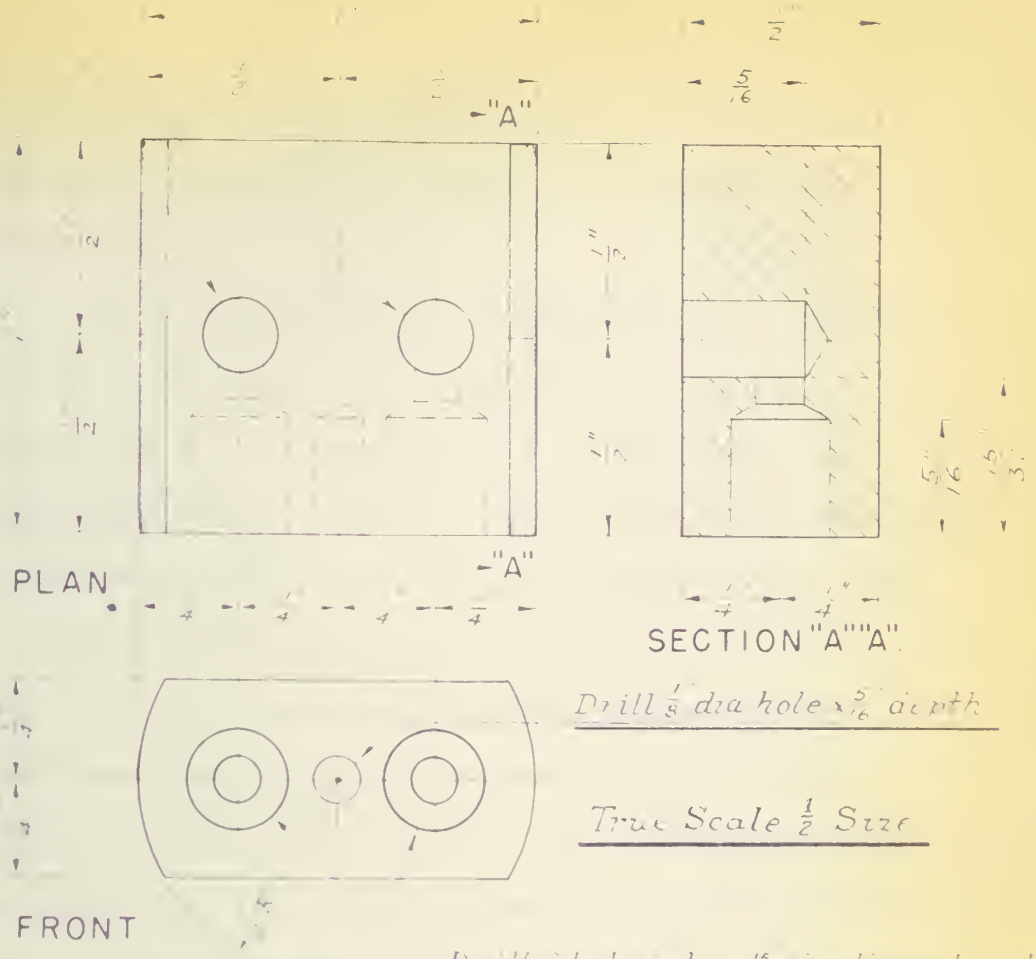
lower the furnace.

C. Specimen Holder and Attachments.

The prime requirement for the specimen holder is that it should be an inert material not affected by repeated heating within the temperature ranges desired and not reactant with the materials that are to be placed in it. It should also be a good thermal conductor and durable enough to withstand repeated cleaning without becoming worn.

Initial experiments were carried out using silica-glass tubes as specimen and inert material holders. These were cut 3 inches long, sealed at one end and placed in holes drilled symmetrically into one end of a solid steel rod which exactly fitted into the furnace liner. This temporary arrangement did not give good results. The tubes became hard to clean, requiring replacement after every two or three runs, and excessive oxidation of the steel block caused scaling on its surfaces. It was therefore decided to use a palladium block, 1 inch by 1 inch by 1/2 inch in size, and machined as shown in figure 3. The thermocouples enter through the openings O_1 and O_2, and the sample and inert material is packed into the thermal recesses on the top of the block.

A search of the literature has shown that most workers favour the use of a nickel or nickel-chrome steel block but ceramic holders have also been widely used, especially for the analysis of reactive sulphides. Palladium, however is a



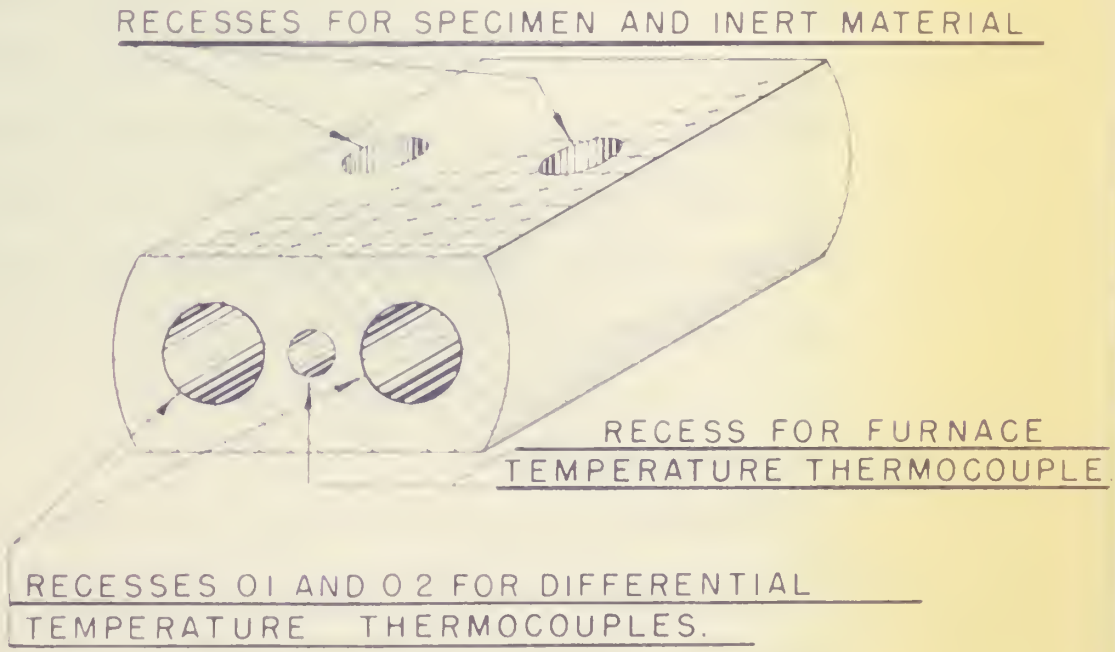


FIGURE 3. PALLADIUM SPECIMEN HOLDER.

particularly inert metal with a melting point of 1555°C. It is easily obtained in Canada and is priced more reasonably than the other noble metals.

The thermocouple wiring diagram is shown in figure 4. Chromel-alumel wires were used to measure the differential temperatures between the specimen and the inert material and a single platinum/platinum-13% rhodium couple measures the temperature of the block itself. The chromel-alumel thermocouples were found to have good sensitivity, were durable and were easily made in the laboratory. Before use, each newly-welded thermocouple was "pre-heated" in a bunsen flame for at least an hour to clean off any borax or carbon adhering to its head. It was found also that time spent in matching thermocouples was well worth-while. This was done quickly by examining the heads under a lower-power microscope in order to select pairs that were of approximately the same size and shape - any small irregularities in the weld being removed later by gentle rubbing with an emery cloth. This precaution was usually enough to ensure that, when heated in the furnace, the thermocouple potentials would balance and a perpendicular base-line would be obtained. In some experiments however, this balance was not achieved and a base-line lying obliquely across the chart resulted.

The specimen holder and thermocouple assembly is shown in plate 2. The thermocouples are shielded by double-holed ceramic insulators and are passed through silica-glass tubes at the closed end of the supporting tray. This tray was cut from

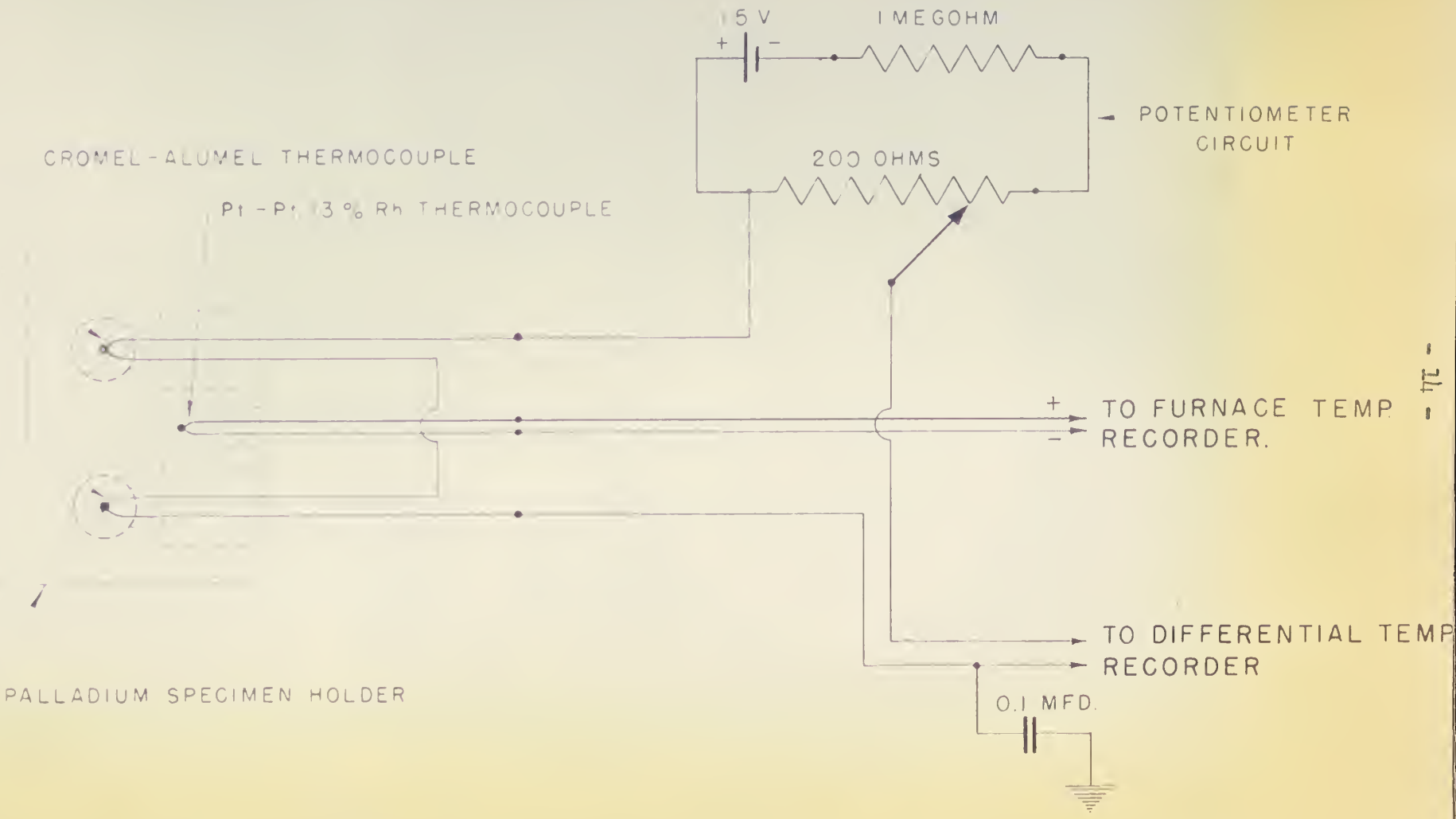


FIGURE 4 THERMOCOUPLE WIRING DIAGRAM SHOWING POTENTIOMETER FOR SHIFTING BASE LINE ON DIFFERENTIAL TEMPERATURE RECORDING CHART.

PLATE 2.
Specimen holder and Thermocouple Assembly.

an alundum tube chosen to fit closely into the furnace liner and the silica-glass tubes were first cemented into place before the end of the tray was completely sealed with a mixture of litharge and glycerine.

D. Program Controlling Unit.

The function of this unit is to give constant rates of heating to the furnace by intermittent application of current to the heating element. The unit consists of four components : a Beck 8101 program controller, a Beck 5781 Putmo (pulse-time modulation controller), a manually adjusted A.T.C. rate controller and a G.E.C. megnetic relay switch.

The rate controller consists of a motor-driven cam operating the power supply for the whole control unit. The cam is adjusted by an exterior knob with a pointer and a dial marked in 1% graduations from 1 to 100% which represent the percent time per minute that the switch will be closed. Thus with the pointer set at 60% on the dial the switch will be closed for 36 seconds of every minute. This intermittent power supply energizes the program controller motor which operates a slide-wire slider to give steady heating at the rate desired.

The Putmo controller regulates the "on" time with respect to the "off" time of power input to the furnace by activating the G.E.C. magnetic switch. A throttling range dial and a sensitivity adjustor are located on the inside panel of the Putmo controller. To control the furnace heating the following

procedure has been found satisfactory:

The rate controller is set to give the desired rate of heating (Figure 5) and the power supply is turned on. With maximum sensitivity and at zero throttling range the furnace temperature will oscillate as control will be at the ordinary "on-off" limits as prescribed by the program controller. The magnitude of this oscillation and the pulse-time period of furnace heating is noted. The throttling range is now set at about 20 and the temperature oscillation will decrease and the time period will become shorter. After noting the improvement, the throttling range is again increased slowly until a linear heating rate is shown on the recorder. The sensitivity is now decreased by turning the sensitivity adjustment counter-clockwise. This will lengthen the pulse-time period of furnace heating, thereby reducing the duty on the mechanical contactors. If the heating rate again oscillates due to this loss of sensitivity then the throttling range may be lowered. This procedure is continued until the longest time period is established that will still result in a smooth heating rate.

Initial experiments showed that for this particular furnace a throttling range setting of 75 and full sensitivity gave best control below 200°C. Above that temperature a setting of 35 on the throttling range and sensitivity adjusted to about three-quarters open gave an excellent heating rate.

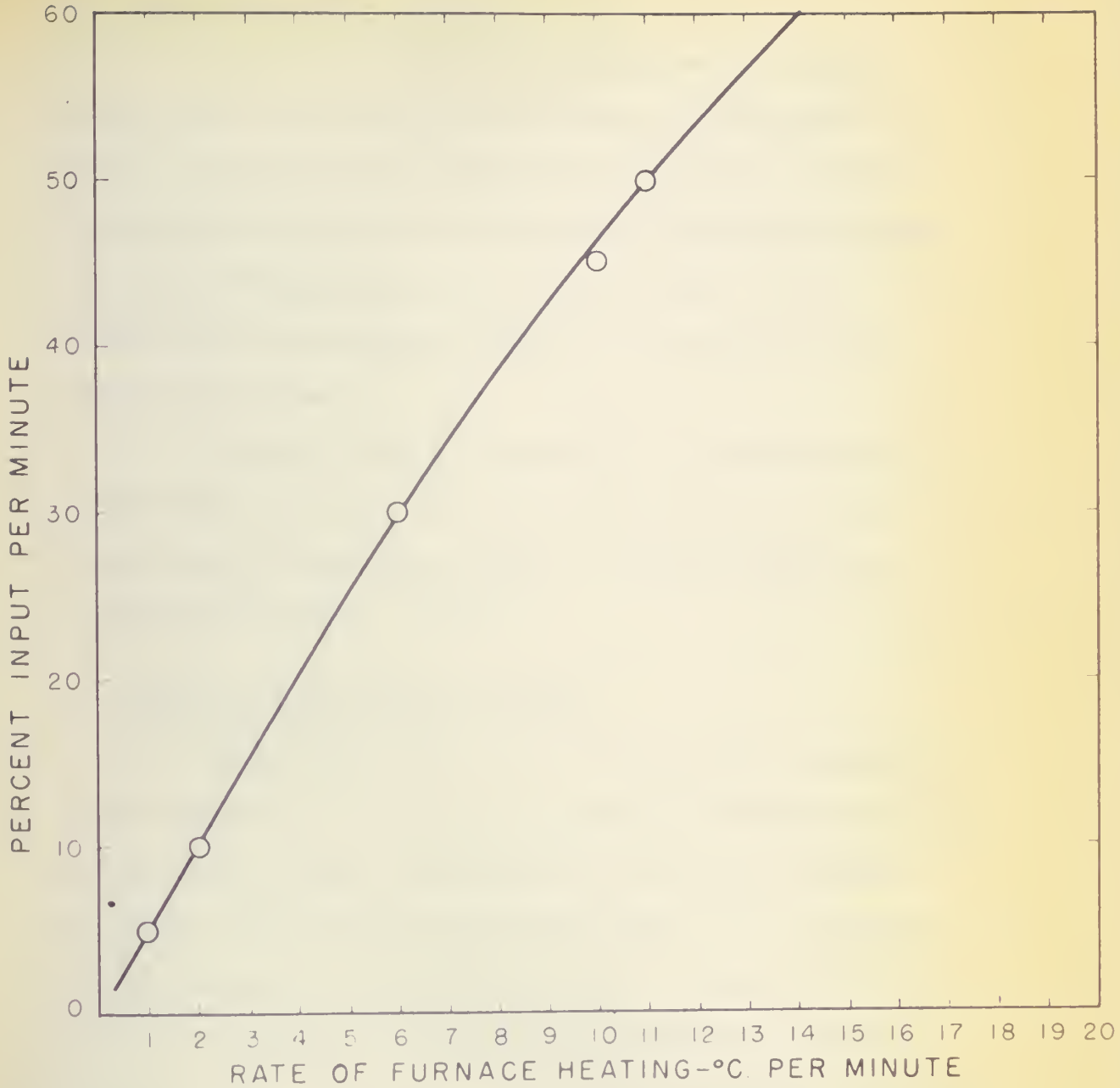


FIGURE 5. A.T.C. CONTROLLER SETTINGS TO GIVE DESIRED RATES OF FURNACE HEATING.

E. Furnace Temperature Recorder.

The furnace temperature recording unit is a Brown Model Y153(R) 10P single record strip chart potentiometer. It gives a continuous record of the furnace temperature indicated by the electrical potential developed in the platinum/platinum-13% rhodium thermocouples in the specimen holder. These thermocouples are connected directly to the recorder by two special alloy wires.

The strip chart is inserted into the recorder on a roller which is geared to move two inches per hour, and the chart itself is conveniently marked in horizontal divisions representing 10 minute intervals.

F. Differential Temperature Recorder.

A Brown Y153 x 12V - x - 6 (V) electronic recorder is used to measure the differences in temperature between the specimen and the inert material indicated by the electrical potentials developed in the chromel-alumel thermocouples. For connecting the thermocouples to the recorder the use of special wire is not necessary, because only differences in electrical potential are being measured. The scale on the instrument is marked in arbitrary units from 1 to 10 on either side of a zero point, and a full scale deflection on one side of this zero point represents the development of an electrical potential of 0.25 millivolts in the thermocouple. For chromel-alumel this potential is the equivalent

of a 5°C differential temperature between the specimen and the inert material as shown in figure 6.

It often happens that the heat evolved by the dissociation of carbonate specimens is greater than 5°C, with the result that the pointer is pushed off-scale. To avoid this a potentiometer was placed in series with the thermocouple circuit (Figure 4). This circuit employs a 1.5 volt Eveready No. 6 dry cell in series with a 1 megohm resistor and a wire-wound 200 ohm potentiometer. When fully open the result is a 0.3 millivolt e.m.f. in the thermocouple circuit:

$$\frac{1.5}{1} = 1.5 \text{ microamps} \quad \text{.....(By Ohms Law)}$$

$$1.5 \times 200 = 300 \text{ microvolts.}$$

$$= 0.3 \text{ millivolts.}$$

Any fraction of this total e.m.f. may be placed in the circuit by moving a voltage divider on the potentiometer. The result is that a zero base-line can be established at any point on the scale and if a carbonate is being analysed enough space can be left on the chart to allow a complete record of the thermal effect to be obtained. This device also permits direct comparisons to be made between thermal curves by first running one specimen then rolling back the chart and shifting the base-line before the second run is made.

The differential recorder is provided with a sensitivity adjustment located inside the instrument. With

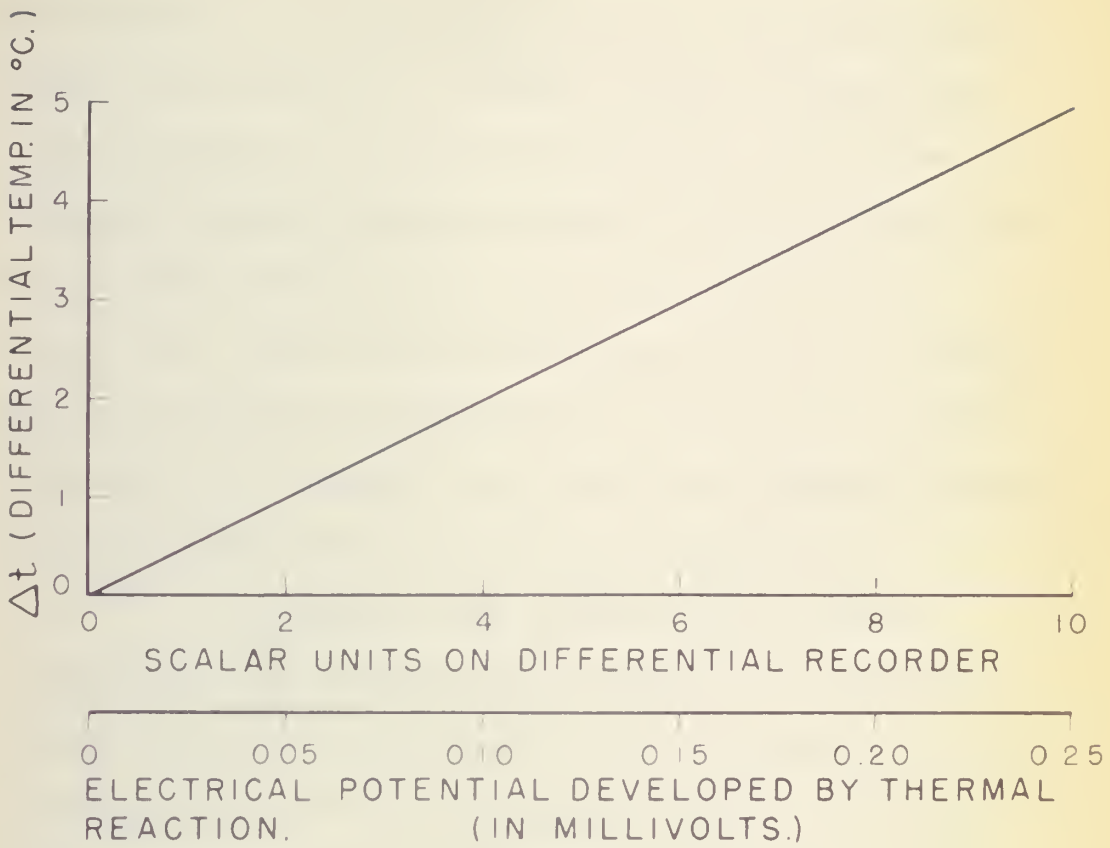


FIGURE 6 RELATIONSHIP BETWEEN DIFFERENTIAL TEMPERATU
AND ELECTRICAL POTENTIAL.

full sensitivity, the thermal curve will have an irregular outline caused by excessive oscillation of the pen. It has been found that a setting of about three-quarters sensitivity will provide the smoothest curve; however, initial experiments showed that oscillations of another type were occuring which bore no relation to the degree of sensitivity. These were momentary horizontal movements sometimes half an inch long and were directly related to the intermittent loading of the furnace coil. These movements were greatly reduced by connecting a 0.1 microfarad condenser between thermocouple and ground (Figure 4), thus bypassing the instantaneous voltage fluctuations that were being induced into the thermocouple circuit.

A schematic wiring diagram for the complete apparatus is shown in figure 7. All connections between the control components and the recorders were made with No. 14 rubber-insulated stranded wire. For the furnace connections No. 10 insulated copper wire was used and in either case all external wiring was shielded in flexible conduit. To permit movement of the furnace, the leads from it to the magnetic relay switch were made of ample length and cut from a heavy stranded copper wire with an asbestos cover.

It will be noted from figure 7 that the two recorders are provided with a separate connection to the 115 volt power line. This allows the electronic amplifiers in the recorders to be kept on continuously as recommended by the

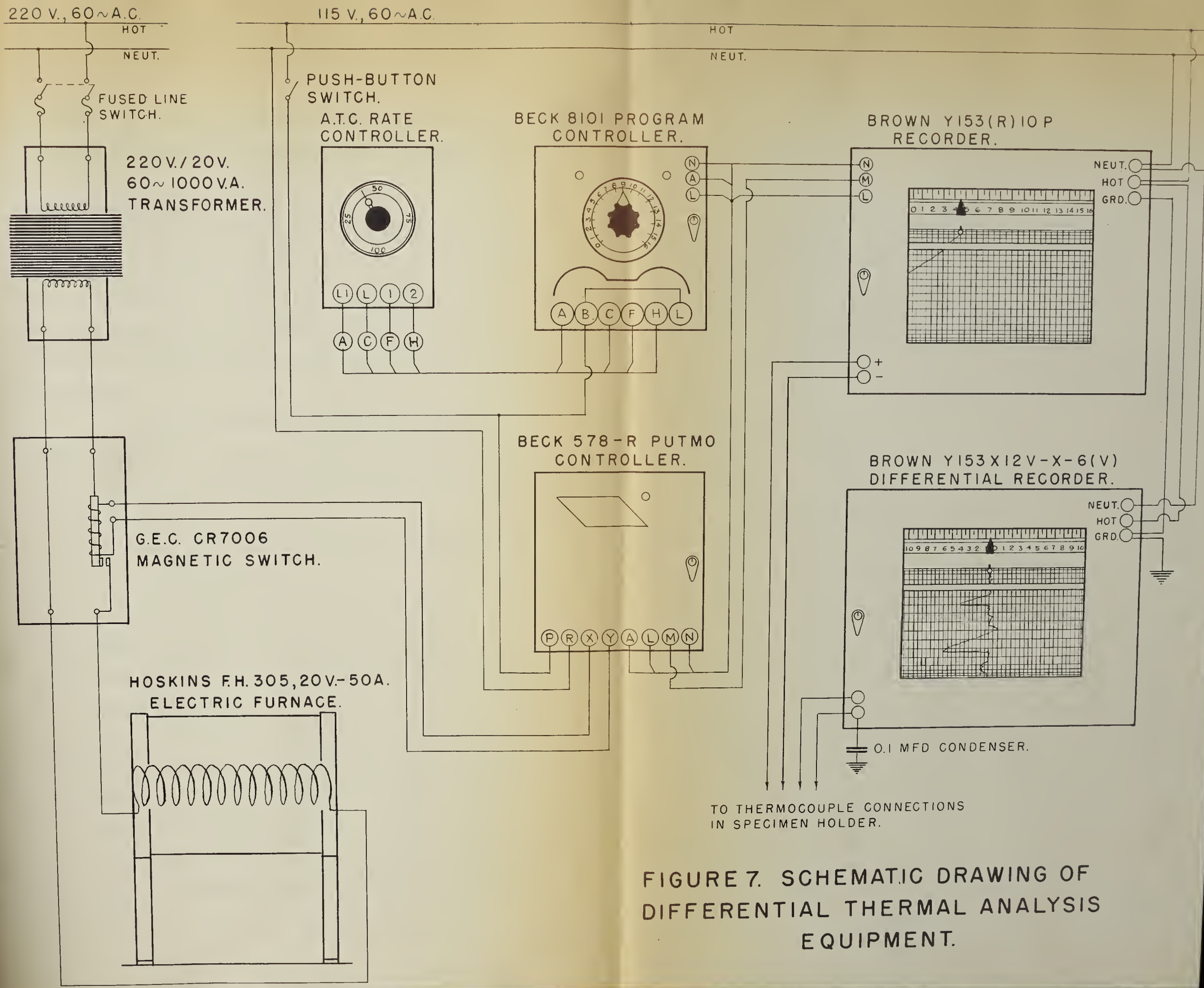


FIGURE 7. SCHEMATIC DRAWING OF DIFFERENTIAL THERMAL ANALYSIS EQUIPMENT.

manufacturers (5). However, separate switches in each recorder provide a means of turning off the chart-drive motors independently.

G. Operating Procedure.

With the specimen and inert material in place in the specimen holder, the thermocouple assembly is checked for short-circuits. The furnace is then slid on to the supporting tray until the specimen holder is in position about 6 inches inside the furnace, and a ceramic plug is fitted into the open end of the furnace liner.

A definite order has been adopted for setting the controls and starting the heating. These are listed as follows:

1. Set the rate controller to give the desired heating rate (Figure 5).
2. Set the program controller to indicate approximately the room temperature.
3. Switch on the chart-drive motors in each recorder.
4. Adjust the thermocouple potentiometer (Figure 4) to bring the differential temperature recording pen to the desired base.
5. Switch on the 220 volt furnace power supply.
6. Switch on the 110 volt power supply to drive the program controlling unit and to activate the magnetic relay switch on the furnace power line.

The furnace will now commence heating. It remains only to adjust the throttling range of the Putmo controller in

order to achieve the smoothest rate of heating possible. This procedure has already been described under a discussion of the program controlling unit, and experimental results have shown that for this equipment the following settings will give a linear heating rate.

Below 200°C - throttling range set at 75.

Above 200°C - throttling range set at 35.

During the short time that differential thermal methods have been applied to the analysis of carbonate minerals it has become apparent that great care and precision is necessary in the preparation of specimens. This aspect is discussed in a later chapter where the effects of various preparation techniques are compared but here only a brief outline of procedure is presented.

The material to be analysed is first ground in a mullite mortar and passed through Tyler screens in order to obtain the desired particle size. A convenient amount is weighed and thoroughly mixed in the desired proportions with a diluent of chemically pure aluminum oxide or fused silica of minus 200 mesh particle size, which also serves as the inert material. The specimen and the inert material are now packed a little at a time into the recesses of the specimen holder; great care being taken to ensure that the thermocouple heads are in complete contact with the materials and that the same degree of packing is achieved with each specimen. These factors are of great importance when

thermal curves are to be compared and when experimental reproducibility is desired.

H. Furnace Temperature Recorder Calibration.

The furnace temperature recorder is provided with a temperature scale which may be read to the nearest five degrees Centigrade; all calibrations therefore fall within this limit. Two methods were used here to check the accuracy of the furnace temperature recorder:

1. By immersing the platinum/platinum-rhodium thermocouple in materials of known melting point, heating in a bunsen flame until fusion occurs and then reading the temperature indicated on the recorder scale. The obvious difficulty was to determine visually the exact point of fusion and to heat the material slowly enough so that this point was not over-reached. The variations between the recorded temperature and the theoretical temperature of fusion (Table 1) indicate that the method serves only as a quick and approximate check. The materials used were ammonium nitrate, silver nitrate and silver iodide, the melting points of which are all below 550°C.

2. A more accurate determination was obtained by using the differential thermal circuit itself to record the inversion points of certain materials and by noting the indicated furnace temperature at which these inversions take place. Barshad (1) explains how this method may be used to indicate the upper and lower limits of any thermal reaction by mixing indicator materials

of suitable inversion points with the specimen to be analysed. This, however, seems unnecessary when the apparatus is designed to give a continuous and fairly accurate record of furnace temperature. It will be seen from tables 1 and 2 and from the thermal curves of the materials used in this calibration, that the temperature recording apparatus in this equipment has an inherent error of only about +10°C in the temperature range above 500°C.

TABLE 1

Results of furnace temperature recorder calibration using substances of known temperatures of fusion.

Substance	True Temp. of Fusion	Recorded Temp. of Fusion	Error
NH_4NO_3	170°C	165°C	- 5°C
NH_4NO_3	170°C	185°C	+ 15°C
$AgNO_3$	212°C	215°C	+ 3°C
$AgNO_3$	212°C	225°C	+ 13°C
AgI	552°C	560°C	+ 8°C
AgI	552°C	570°C	+ 18°C

TABLE 2

Results of furnace temperature recorder calibration using d.t.a. of materials of known inversion points.

Specimen Substance	Diluent in Specimen	Inert Material	True Inversion Temp.	Recorded Inversion Temp.	Error
Ag_2SO_4	50%Al_2O_3	Al_2O_3	432°C	430°C	- 2°C
Ag_2SO_4	75%Al_2O_3	Al_2O_3	432°C	435°C	+ 3°C
Quartz	none	Al_2O_3	573°C	583°C	+ 10°C
Quartz	none	Al_2O_3	573°C	583°C	+ 10°C
Quartz	none	Al_2O_3	573°C	585°C	+ 12°C
K_2SO_4	50%Al_2O_3	Al_2O_3	583°C	595°C	+ 12°C
K_2SO_4	75%Al_2O_3	Al_2O_3	583°C	598°C	+ 15°C
K_2SO_4	75%Al_2O_3	Al_2O_3	583°C	595°C	+ 12°C

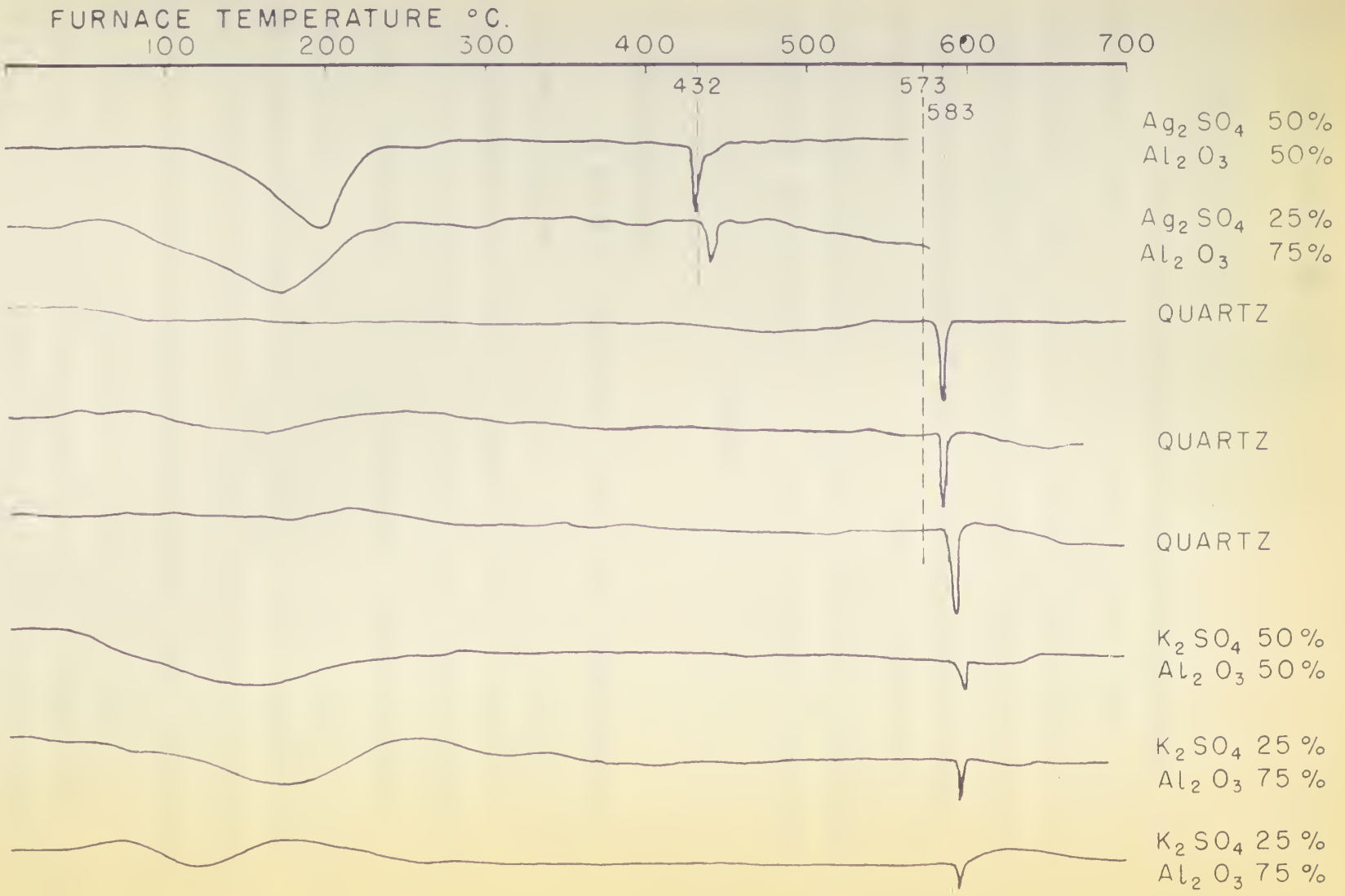


FIGURE 8. THERMAL CURVES SHOWING INVERSION POINTS USED IN CALIBRATION OF FURNACE TEMPERATURE RECORDER.

III. EXPERIMENTAL PROCEDURES

A. General Statement.

There are many parameters affecting the precision and reproducibility of d.t.a. curves which have not yet been fully investigated. These are, rate of heating, particle size of the specimen, dilution of the specimen and the nature of the furnace atmosphere. As the optimum curve for any particular substance is dependent to some degree on all of these variables they must be taken into account before a standard curve can be established. Furthermore, the standard d.t.a. curve so obtained is valid only for one particular set of experimental conditions.

B. Particle Size.

A reaction mechanism for the thermal decomposition of a chemical compound is postulated by Roginskii and Shultz (17). They suggest that decomposition starts at definite reaction centres on the surfaces of each crystal and spreads throughout the crystal. Two phases in this mechanism are distinguished: an initial phase of increasing velocity when reaction zones are small and can grow unhampered in all directions, and a secondary phase of decreasing velocity when the entire surface layer is decomposed and the reaction can progress only toward the centre of the crystal. This postulation is supported by the recent x-ray studies of Wilsdorf and Haul (21) on the dolomite thermal decomposition. Here, the x-ray pattern for dolomite gradually decreased but became more

distinct, indicating that the reaction proceeds from the surface to the interior of the crystal - an ever-decreasing dolomite kernel remaining.

A finely-ground carbonate specimen should therefore decompose completely at a lower temperature than would a coarsely-ground one because there is a smaller temperature differential between the surface and the centre for smaller particles than for larger ones. A secondary factor is the relative thinness of the layer of already dissociated material on a small particle through which CO_2 from the centre of the particle has to diffuse in order to escape. The thermal curves for dolomite specimens of different particle size obtained by Graf (8) supports this postulation. He shows that there is an increase in separation of the two dolomite peaks when the particle size is decreased.

C. Dilution.

The mixing of a mineral specimen with a chemically inert diluent is a useful technique. Firstly, it allows the complete thermal record of the specimen to be accomodated on the chart without reducing the sensitivity of the thermocouple circuit and also eliminates the danger of losing a part of the specimen because of a vigorous thermal reaction. A secondary effect of dilution is that of lowering the partial pressure of CO_2 within the inter-granular spaces of the specimen which results in a lowering of the dissociation temperature.

No standard procedure for dilution has so far been published,

probably because there is an optimum dilution for each type of specimen. In the experiments to be described later either alundum powder (Al_2O_3) or silica glass powder (SiO_2) were used in the ratio of 30% by weight of the specimen.

D. Furnace Atmosphere Control

The organic matter present in clays and other sediments often prevents identification of the mineral content of these materials. This is because the broad exothermic effects resulting from the oxidation of the organic matter tends to obscure the more determinative endothermic reactions. If an inert gas such as nitrogen is allowed to flow through the furnace this oxidation will be suppressed and a thermal curve will be obtained which shows only the endothermic peaks.

In the analysis of carbonates, a technique has been developed whereby an atmosphere of CO_2 is introduced into the furnace. Rowland and Lewis (16) report that when calcite is heated in CO_2 at approximately one atmosphere pressure its dissociation is not registered until a temperature of 925°C is reached, but when heated in air the decomposition begins at about 650°C. The equilibrium constant for the reaction $CaCO_3 \rightleftharpoons CaO + CO_2$ (heated in air at one atmosphere) is expressed as

$$Kp = \frac{pCO_2 \times pCaO}{pCaCO_3} \quad \text{(At any given temperature)}$$

and as the partial pressure for the solid state is a constant this can be written $Kp = pCO_2$.

This phenomenon finds application in the thermal analysis of dolomitic limestone. When this material is heated in air the endothermic peak corresponding to the first stage in the dolomite dissociation occurs at about 760°C and is closely followed by the endothermic peak relating both to the second stage of the dolomite dissociation and to the dissociation of $CaCO_3$ as well. When this material is heated in an atmosphere of CO_2 the two peaks become separated (see chapter V).

Experimental work concerning the decomposition of dolomite under low pressure of CO_2 undertaken by Haul and Heystek (9) show how its two endothermic peaks may be made to merge between 700°C and 800°C.

E. Rate of Heating.

In so far as the published d.t.a. curves are concerned, rate of heating has not been rigorously investigated. At slow rates of heating thermal peaks lose their sharpness and become broad loops, an effect as undesirable as that resulting from fast heating which sometimes obscures the character of the thermal curve. Most investigators seem to favour a rate of about 12°C per minute but this may be an outcome of the earlier work done on clays.

Wittles (22) found that some regular relation exists between rate of heating and the corresponding thermographic response (i.e. peak area) for a given energy change. A heating rate of 30°C per minute gave the largest peak areas while slower rates gave progressively smaller peak areas. It is not stated what effect the fast rates had on the character of the curve, but

from this present investigation it will be seen that fast heating results in a loss of detail.

IV. PEAK AREAS.

A. General Statement.

The dependence of the peak area of a thermal curve upon the heat effects caused by an endothermic reaction has been derived theoretically be several investigators. Kerr et al. (13) have shown that since the heat of reaction for a particular change in a mineral is a constant, then the area of the peak corresponding to this change should be proportional to the concentration of the reacting mineral. This relationship forms the basis for the semi-quantitative use of d.t.a., but there are several other factors which must be considered:

1. The thermal conductivity of the specimen is not a constant and may change as the reaction proceeds, due to atomic re-arrangement and the evolution of gases. When the specimen is very small the temperature variations so caused may be ignored.

2. The peak area representing a reaction is affected by various factors inherent in the d.t.a. apparatus such as rate of heating, nature of the sample holder, size of the recesses for the specimen and the inert standard, nature of the thermocouples and the sensitivity of the differential temperature recorder. It is also affected by the physical conditions - particle size, packing, etc., - existing in the specimen itself.

3. The nature of the differential curve is such that it makes difficult the formulation of any one valid procedure for the construction of the base-line which will define the peak area.

Therefore, if a calibration curve is prepared showing area of peak versus percentage for a set of known mixtures, then determinations for an unknown may be made by direct comparison - provided only that the conditions existing in the d.t.a. apparatus, and in each specimen, at the time of calibration are maintained during analysis of the unknowns. Kerr et al. (13) point out that a calibration curve of amplitude versus percentage is more practical since the amplitude may be easily read to the desired accuracy while the area must be laboriously computed. However, as the area is not proportional to the amplitude the amplitude-percent curve will not be linear and may serve only as an approximate measure of concentration.

B. Peak Area Measurement.

If the differential curve after the thermal effect is a direct continuation of the record taken before, the upper boundary of the peak may be obtained simply by drawing a line to connect the points at which deviation began and ended. For this simple case Rowland and Lewis (15) suggest that the points to be joined should be those at which a line at 45° to the base is tangent to the maximum "inflection" of the beginning and ending of the peak.

As such symmetrical peaks are not the rule it is important to adopt some other standard procedure for de-limiting the peak areas.

Sometimes in the process of reaction the conditions of heat transfer in the specimen may be altered. Loss in weight due to dissociation or dehydration will decrease the specific heat of the specimen and consequently lead to a small elevation in its temperature.

On the thermal curve this will have the effect of shifting the base-line toward the exothermic side, but still keeping it parallel to its original direction. For this type of peak the area has been defined in the following manner by Berg (4).

A line is drawn through the point of maximum deviation of the differential curve, perpendicular to the time axis. The linear direction of the curve which established itself after the reaction is produced to intersect this perpendicular. This point is then joined by a straight line to the point where the curve first began to deviate. The area so enclosed is taken arbitrarily as the peak area.

V. DIFFERENTIAL THERMAL ANALYSIS OF DOLOMITIC LIMESTONES.

A. General Statement.

The mineral dolomite, $CaMg(CO_3)_2$, is a ubiquitous component of many sedimentary lime rocks. The description and naming of these rocks in the past has been based mainly on field tests corroborated by occasional chemical analyses and more rarely by optical or x-ray studies. While field tests have been proved sufficient for broad stratigraphic considerations, a rapid method of obtaining closer control is necessary when carbonate rocks are to be studied with a view to their economic value. This can be achieved rapidly by d.t.a. and it is a purpose of this thesis to set up a series of standard thermal curves for a rock containing varying percentages of dolomite and to relate these percentages to the peak area of the lower-temperature dolomite dissociation.

The thermal dissociation of calcite into CaO and CO_2 at one atmosphere pressure begins at about 670°C and ends abruptly near 890°C. The d.t.a. curve for this reaction shows a broad endothermic loop which at first deviates very gradually and then becomes considerably sharper after 850°C. The thermal decomposition of dolomite, on the other hand, takes place in two stages, which, on the d.t.a. curve are shown as a well-defined endothermic peak occuring between 750°C and 800°C and a broader peak occurring between 850°C and 910°C. The d.t.a. curve of a dolomitic limestone is therefore made up of the broad endothermic loop corresponding to the dissociation of calcite, upon which are superimposed the two peaks reflecting the successive stages in the

dolomite dissociation.

The nature of the dolomite thermal dissociation is not precisely known. A simple explanation for the two dissociation stages, offered by Berg (3), is the primary decarbonation of the $MgCO_3$ part of the dolomite followed by the dissociation of CO_2 from the $CaCO_3$ part of the dolomite. A more recent explanation put forward by Willsdorf and Haul (21) involves the preliminary dissociation into oxides followed by a recombination, $CaO + CO_2 \rightleftharpoons CaCO_3$, prior to the final dissociation. This may be written:

$$MgCa(CO_3)_2 \rightleftharpoons MgO + CO_2 + CaCO_3$$
$$CaCO_3 \rightleftharpoons CaO + CO_2$$

A recent report by Rowland and Beck (15) shows how small quantities of dolomite may be determined by measurement of the d.t.a. peaks; and calibration curves are presented which plot percentage dolomite against peak area - although no mention is made of the attendant variables. In this present investigation it has become apparent that a plot of peak area versus percentage is meaningful only for a given set of conditions where the specimens are all packed to the same degree into the specimen recess and where the particle size is constant for all the specimens.

B. Preliminary Experiments.

Several preliminary runs were made using differing conditions of furnace atmosphere and varying amounts of diluent. These served in the early stages of the investigation as a means of observing the response of the apparatus and for establishing a satisfactory standard procedure which would result in expermental reproducibility. The

thermal curves so obtained are shown in Appendices 2 and 3.

Curves 8 and 9 represent the dissociation of a channeled sample of Devonian limestone taken from Pochantas quarry, Jasper Park. The specimens ground to pass a 100 mesh screen, were not diluted and were run at a heating rate of 16°C per minute. The peak at 575°C is due to the inversion of quartz which was used as the "inert" standard in order to check the calibration of the furnace temperature scale, and the inversion effect is therefore shown as an exothermic one. Note that there is a suggestion of an endothermic reaction between 750°C and 850°C which might be due to the initial stage in the dissociation of dolomite.

Curves 10 and 11 show the dissociation of the same limestone under the same experimental conditions with the exception of heating rate which was lowered to 13°C per minute. A definite endothermic effect corresponding to the lower temperature dolomite dissociation is recorded between 750°C and 850°C. A smaller deflection at about 790°C reflects the superimposition of the peak corresponding to the dissociation of the $CaCO_3$ part of the dolomite upon the already established calcite peak.

Curve 16 shows the thermal dissociation of a dolomite crystal from Kicking Horse Pass, run at a rate of about 20°C per minute.

The detail recorded in all these curves is affected by a heating rate which was too fast, with the result that they are of little value for quantitative interpretation. Lack of diluent in the

specimen also caused peaks which were too large for the chart and therefore could not be areally measured.

The curves in Appendix 3 show the dissociation of synthetic mixtures of calcite and dolomite diluted with fused silica glass and all ground to pass a 200 mesh screen. Heating rates of between 6°C and 10°C per minute were used. In an attempt to separate the endothermic effect due to the first stage in the dolomite dissociation from the higher temperature $CaCO_3$ dissociation effects, an atmosphere of CO_2 was introduced into the furnace. The flow of CO_2 was controlled by a regulator delivering about half a liter of gas per minute at atmospheric pressure. A small asbestos baffle, placed into the furnace tube at the point of gas delivery, allowed the gas to heat to furnace temperature before it reached the specimen block. This avoided undesirable cooling effects.

In each run the two endothermic effects were well separated but good reproducibility was not attained and the peak area corresponding the first stage of dolomite dissociation became difficult to measure with any degree of accuracy. The lowered rates of heating as compared to those of earlier runs resulted in straighter base lines.

With the accumulated experience and operating technique acquired from these experiments it was decided to adopt the standard procedure described in the next chapter for the analysis of the dolomitic limestones and synthetic mixtures.

C. Experimental Procedure.

The object of these experiments was to determine the relationship between the percentage dolomite in a specimen and the

peak area representing the thermal dissociation of the $MgCO_3$ part of that dolomite. Three separate series of experiments were undertaken using synthetic mixtures of calcite and dolomite, naturally occurring dolomitic limestones and commercially obtained standards of dolomitic limestones. All runs in series 1 and 2 were made under identical experimental conditions, the only variable being the actual weight of specimen introduced into the furnace. For series 3, new thermocouples were installed but great care was taken to obtain the same degree of symmetry in their placement as with the previous series. A heating rate of 6°C per minute was adopted throughout.

D. Materials Used.

Series 1. (Appendix 4)

The materials used were obtained from a single rhombohedral crystal of optically pure Iceland spar ($CaCO_3$) and a crystalline mass of opaque dolomite ($CaMg(CO_3)_2$) of determined chemical purity:

	Dolomite sample	Theoretical
$CaCO_3$	54.50%	54.35%
$MgCO_3$	44.71%	45.65%

The two minerals were ground in a mullite mortar to pass a 200 mesh Tyler screen and were mixed in varying proportions. Each sample was then diluted with 30% by weight of ground silica glass, also of -200 mesh particle size, and again thoroughly mixed. Table 3 presents the data for the mixtures so obtained.

TABLE 3

Data for Series 1.

Specimen No.	% dolomite in specimen	Calc.Weight of dolomite in specimen	% diluent, SiO_2, in specimen	Total Weight of specimen	Peak Area of 1st dolomite dissociation
85	1.54	0.005 gms.	30	0.35 gms.	---
81	1.92	0.006 "	30	0.35 "	0.3 cms^2
80	3.84	0.013 "	30	0.35 "	0.6 "
74	7.68	0.027 "	30	0.35 "	1.1 "
114	11.54	0.041 "	30	0.36 "	1.6 "
76	15.36	0.054 "	30	0.35 "	2.2 "
115	19.23	0.067 "	30	0.35 "	2.6 "
113	23.07	0.081 "	30	0.35 "	3.5 "
77	30.72	0.108 "	30	0.35 "	5.1 "
96	32.8	0.115 "	30	0.35 "	5.2 "
95	38.46	0.134 "	30	0.35 "	6.2 "
97	49.14	0.172 "	30	0.35 "	8.6 "

Series 2. (Appendix 5)

The samples were obtained from diamond drill cores of Devonian strata forming an upthrust fault-block in the foothills of west central Alberta, and had been chemically analysed for the constituents critical in the manufacture of cement (Appendix 1). They were ground to pass a 200 mesh Tyler screen and were diluted with 30% by weight of ground silica glass of -200 mesh size. Data

for this series is presented in table 4.

TABLE 4

Data for Series 2.

Specimen No.	% MgO in Carbonate sample	Calc. % dolomite in specimen	Calc. wt. dolomite in specimen	% diluent, SiO_2, in specimen	Total wt. of specimen	Peak Area of 1st dolomite dissociation
93	1.03	3.42	0.012 gms.	30	0.351 gms.	0.2 cms^2
92	2.02	6.28	0.022 "	30	0.350 "	0.6 "
90	5.75	18.18	0.064 "	30	0.352 "	2.2 "
112	7.46	24.17	0.086 "	30	0.360 "	3.0 "
89	9.38	31.18	0.106 "	30	0.340 "	4.2 "
110	13.21	41.94	0.151 "	30	0.360 "	7.4 "
88	16.00	51.14	0.179 "	30	0.350 "	8.3 "
121	16.00	51.14	0.179 "	30	0.250 "	8.3 "
87	16.79	53.71	0.188 "	30	0.350 "	9.6 "

Series 3. (Appendix 6).

These samples were supplied by the Chemistry Department of the University of Alberta. The same procedures of grinding and diluting described above were carried out for each sample and the data for this series is presented in table 5.

TABLE 5

Data for Series 3

Specimen No.	% MgO in Carbonate sample	Calc. % dolomite in specimen	Calc. wt. dolomite in specimen	% diluent, SiO_2, in specimen	Total wt. of specimen	Peak Area of 1st dolomite dissociation
108	4.53	14.23	0.037 gms.	30	0.26 gms.	0.85 cms^2
107	9.08	28.46	0.074 "	30	0.26 "	2.5 "
106	13.67	43.46	0.113 "	30	0.26 "	3.9 "
105	21.82	69.61	0.181 "	30	0.26 "	6.5 "

E. Discussion.

The volume of the thermal recess for the specimen is a constant only for a particular setting of the thermocouples and thermocouple insulators. Each time the thermocouples are renewed this volume may be changed because of variations in the placement of the insulating rods into the specimen block. For carbonate analyses, thermocouple renewal need not be frequent and, in fact, the same thermocouples were used for the analyses of all the specimens of the first two series of standards. Cleaning the specimen recess after each run can be done without disturbing the thermocouple assembly, merely by loosening the specimen with a needle and blowing away the powder with a jet of compressed air. The actual weight of diluted sample being placed in the specimen recess was therefore determined in each case by weighing the amount of excess sample before and after each filling of the specimen recess.

In order to calculate the weight of dolomite in each specimen of series 2 and 3, it is necessary to assume that all the MgO determined by chemical analysis represents magnesium from the mineral dolomite. That none of it was in the form of magnesite is indicated by the lack of any endothermic deflection near 500°C corresponding to the dissociation of this mineral; and the small silica content determined in the chemical analyses of series 2 precludes its presence in these specimens, as the magnesium of a magnesium silicate. There still remain, nevertheless, two further possibilities for error arising from this assumption. Firstly, brucite ($MgO(OH)_2$) and periclase (MgO) may have been present in the samples; these minerals, however, are not common constituents of sedimentary carbonates. Secondly, magnesium may have been present to some unknown limit, as an ionic substitution of Mg for Ca in the calcite lattice.

The chief difficulty in accurate areal measurement of the thermal peak is connected with the construction of the straight line that closes the peak; and for comparison purposes the same procedure must be rigorously applied in all instances. The procedure described in chapter 5 was found to be unsuitable due to the superimposed character of the first dolomite dissociation peak. However, as all the thermal curves showed excellent reproducibility of form, closure was effected simply by extending the direction of the line which had established itself before the dolomite decomposition, to intersect with the return slope of the first peak. The area so enclosed was measured with a planimeter

set to read directly in square centimeters, and each measurement was repeated at least five times in order to obtain an average reading.

Figure 9 shows a plot of the peak area corresponding to the first stage in the dolomite dissociation,

$$CaMg(CO_3)_2 \rightleftharpoons CaCO_3 + MgO + CO_2 ,$$

and the calculated percent by weight of dolomite in the specimen. The plots for both the synthetic mixtures and the natural carbonate samples show a direct proportionality between the area of the peak and the percentage of dolomite in the specimen.

The difference between the two curves S1 and S2 is almost a constant and indicates that the naturally occurring carbonate specimens of series 2 have a small excess of magnesia which was not in the form of dolomite. It should be stated, also, that as the chemical analysis of the dolomite used in the synthetic mixtures of series 1 shows a small deficiency from the theoretical $MgCO_3$ content (0.94%), then the difference between the two curves S1 and S2 should actually be increased by a correspondingly small amount.

The plots along the curve S3 are obtained from the d.t.a. of series 3. These specimens were run under conditions different from those of the previous two series, in that new thermocouples were installed and that the actual weights of the specimen were reduced. The direct proportionality between percentage dolomite and peak area of the lower-temperature dolomite dissociation is still preserved, but the deviation of this curve from those of the previous series is very marked. The fact that the chemical control for recasting the dolomite content of this series was not as complete as that obtained for series 2, together with the high silica content

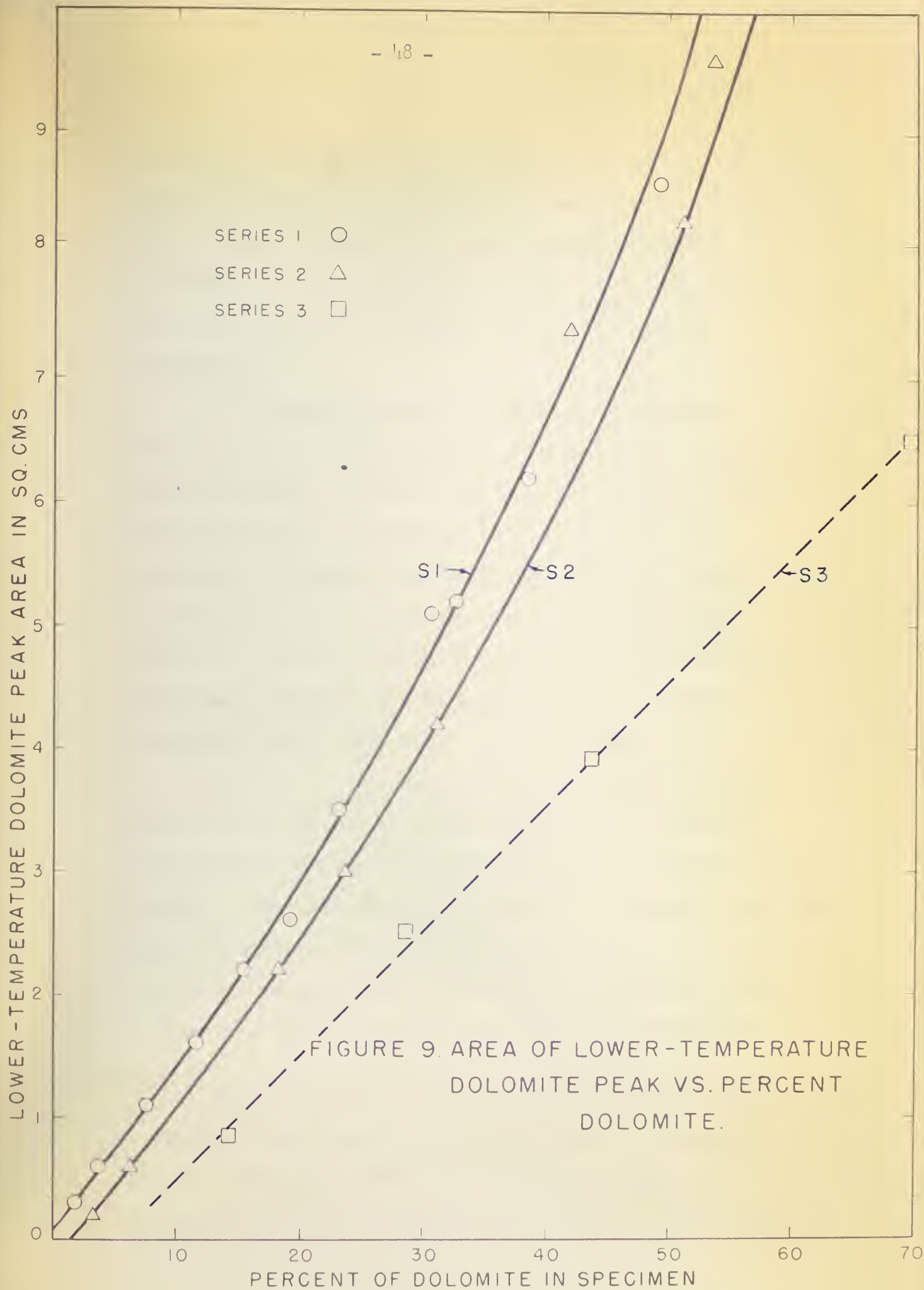


FIGURE 9. AREA OF LOWER-TEMPERATURE DOLOMITE PEAK VS. PERCENT DOLOMITE.

of these specimens may be partly responsible for the high values of the calculated dolomite percentages. The only other conspicuous factor that can be examined in order to explain this deviation is the difference in weight between specimens of this series and those of the others, but as will be shown below, this factor is insignificant.

The thermocouple head, around which the specimen is packed, has a theoretical maximum range in sensitivity beyond which temperature changes will not be recorded. Thermographic response of the thermocouple will therefore be a function only of the concentration of reactant material within this range. Therefore, if different amounts of a particular specimen are analysed under constant conditions of particle size and packing, then the thermographic response should remain a constant as long as the mass of the specimen does not fall below a certain minimum.

In order to test this postulation, five runs were made using decreasing weights of specimen No.115, and the peak areas corresponding to the first stage in the dolomite dissociation were measured. These values when plotted against the weights of specimens (Figure 10) indicate that the thermographic response is a constant for specimens weighing more than 0.23 gms. For specimens weighing less than this amount, the peak areas become progressively smaller.

The possibility of silicate reactions occurring between Ca and Mg carbonate and the silica diluent has been considered. Appendix 9 (following Appendix 1) reviews this problem, and it is shown that the $MgCO_3$ concentration is not involved in such reactions.

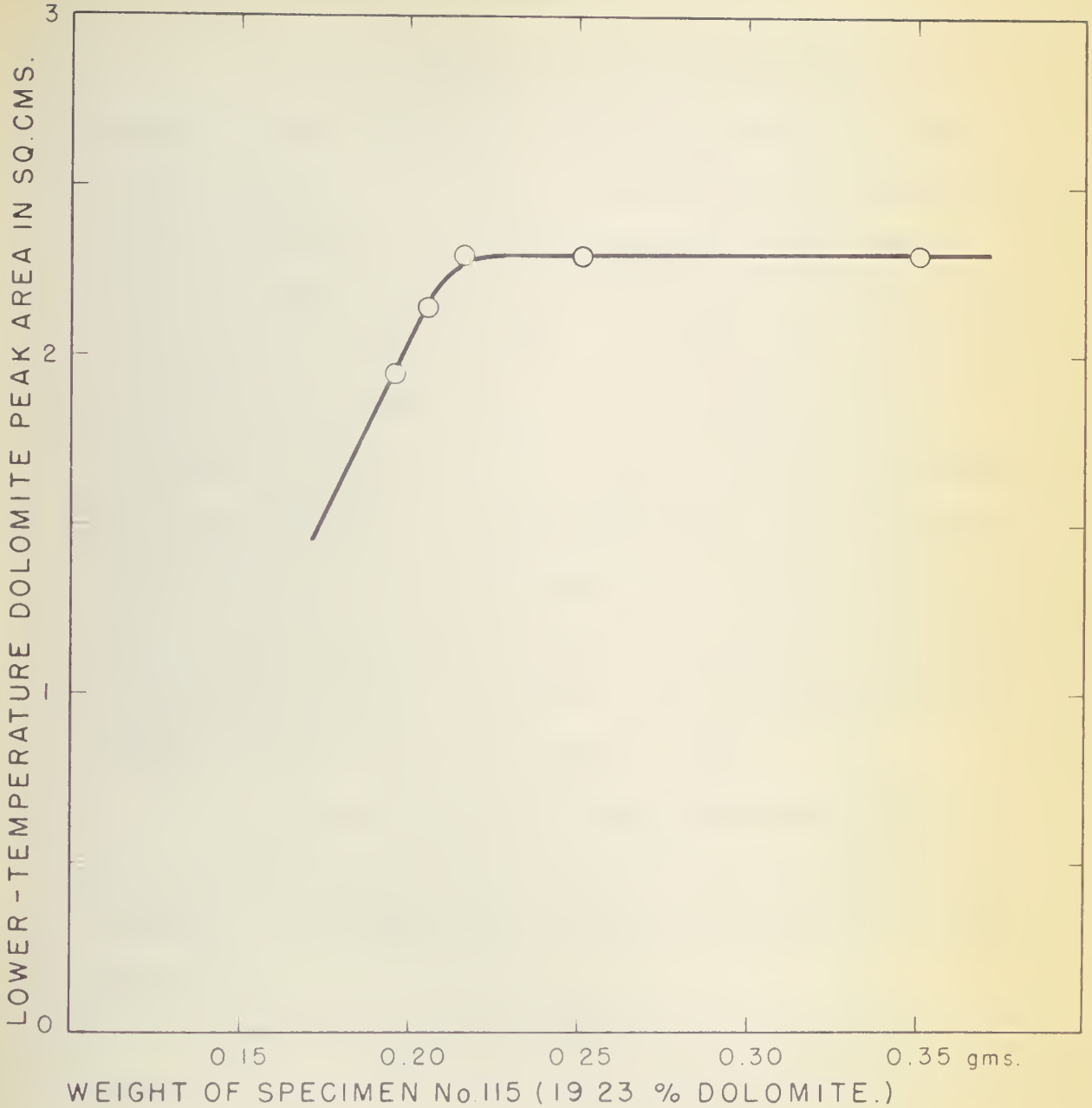


FIGURE 10. PEAK AREAS VERSUS WEIGHT OF SPECIMEN.

VI. THERMAL DISSOCIATION OF LEAD CARBONATE AND MAGNESIUM CARBONATE

A. General Statement.

On heating carbonates, a condition of equilibrium is normally attained: $MCO_3 \rightleftharpoons MO + CO_2$; and if the CO_2 can escape it will be driven off completely when its dissociation pressure exceeds the pressure of CO_2 in the atmosphere. This system is not always simple, and d.t.a. can substantiate the chemical data in showing that the carbonate and the oxide may give a series of solid solutions in which the CO_2 pressure becomes smaller the richer they are in oxide. This concept has been of long standing yet thermal curves have been published which do not agree with it. These curves are of the systems $PbCO_3$ - PbO and $MgCO_3$ - MgO as represented by the minerals cerrusite and magnesite. Experiments in the d.t.a. of these minerals were therefore carried out in an attempt to obtain more precise thermal curves.

A review of the chemical data pertaining to these carbonate systems shows evidence for the existence of oxy-carbonates as definite intermediate products which form during their thermal dissociation.

In 1925, by heating a known weight of $PbCO_3$ under a known pressure of CO_2, Tzentnershver et al. (20) measured three breaks in the pressure-temperature curve indicating the successive formation of the oxy-carbonates $3PbO.5PbCO_3$, $2PbO.PbCO_3$ and $PbO.PbCO_3$. In a similar study of $MgCO_3$ he concluded that the successive steps in

its dissociation yield the products $MgO.3MgCO_3$, $3MgO.MgCO_3$ and $4\ MgO_3$ between 373°C and 469°C. In the dissociation of a specimen of rhombobedral magnesite Tzentnershver and Bruzs (19) determined the following stages.

$$402°C - 4\ MgCO_3 \rightleftharpoons MgO.3MgCO_3 + CO_2$$

$$437°C - MgO.3MgCO_3 \rightleftharpoons 2(MgO.MgCO_3) + CO_2 \text{ or}$$

$$2MgCO_3 \rightleftharpoons MgO.MgCO_3 + CO_2$$

$$480°C - MgO.MgCO_3 \rightleftharpoons 2MgO + CO_2$$

In 1951, magnesite was tested by weight loss and d.t.a. by Sersale (18) for the detection of hydroxide or basic carbonates. The chief reactions by loss of CO_2 were observed at 580°C and 620°C. For a sample of magnesite associated with brucite and basic carbonates the first thermal effect was noted near 450°C and the second at 600°C. Sersale suggests that this is indicative of a loss of CO_2 and H_2O in three steps:

$5\ MgO.4CO_2.5H_2O$ - Stable up to 260°C.

$5\ MgO.3CO_2.3H_2O$ - " " " 400°C.

$5\ MgO.1\ 1/2CO_2$ - " " " 500°C.

as intermediate phases with distinct reaction effects.

The International Critical Tables (10) list three reactions in the thermal dissociation of $PbCO_3$. These are:

$$216°C - 268°C ; \quad 2PbCO_3 \rightleftharpoons PbO.PbCO_3 + CO_2$$

$$268°C - 351°C ; \quad 3(PbO.PbCO_3) \rightleftharpoons 2(PbCO_3.2PbO) + CO_2$$

$$338°C - 405°C ; \quad PbCO_3.2PbO \rightleftharpoons 3PbO + CO_2$$

B. Previous Studies on the d.t.a. of Cerrusite.

In 1947 Cuthbert and Rowland (6) published a thermal curve for cerrusite at a heating rate of 10°C per minute which showed three endothermic reactions. These they considered to be an indication of the three steps in the dissociation of $PbCO_3$ outlined by Tzentnershver. From figure 11, however, it will be seen that only two of these endothermic reactions occur in the temperature range 250°C - 450°C. The third occurs at 860°C, some 400° higher than the $PbCO_3$ dissociation range listed by either Tzentnershver or in the International Critical Tables.

In 1950, Beck (2) obtained a thermal curve for cerrusite, at an unspecified heating rate, which showed decomposition taking place in two stages between 320°C and 510°C. He reported no endothermic effect at high temperature and showed by an x-ray picture of the product at 550°C that all the cerrusite had decomposed to PbO.

The thermal curve for cerrusite (Figure 11) obtained by Kauffman and Dilling (11) at a heating rate of 10 - 12°C, shows three endothermic reactions, one of which is represented by a subdued and ill-defined peak. These occur between 300°C and 500°C and bear a closer relationship to the chemical data. The beginning of a fourth endothermic peak at 850°C, which corresponds to the third peak obtained by Cuthbert and Rowland, is attributed to the melting of lead oxide.

C. Experimental Procedure and Discussion of Results.

A coarsely crystalline specimen from the mineralogical

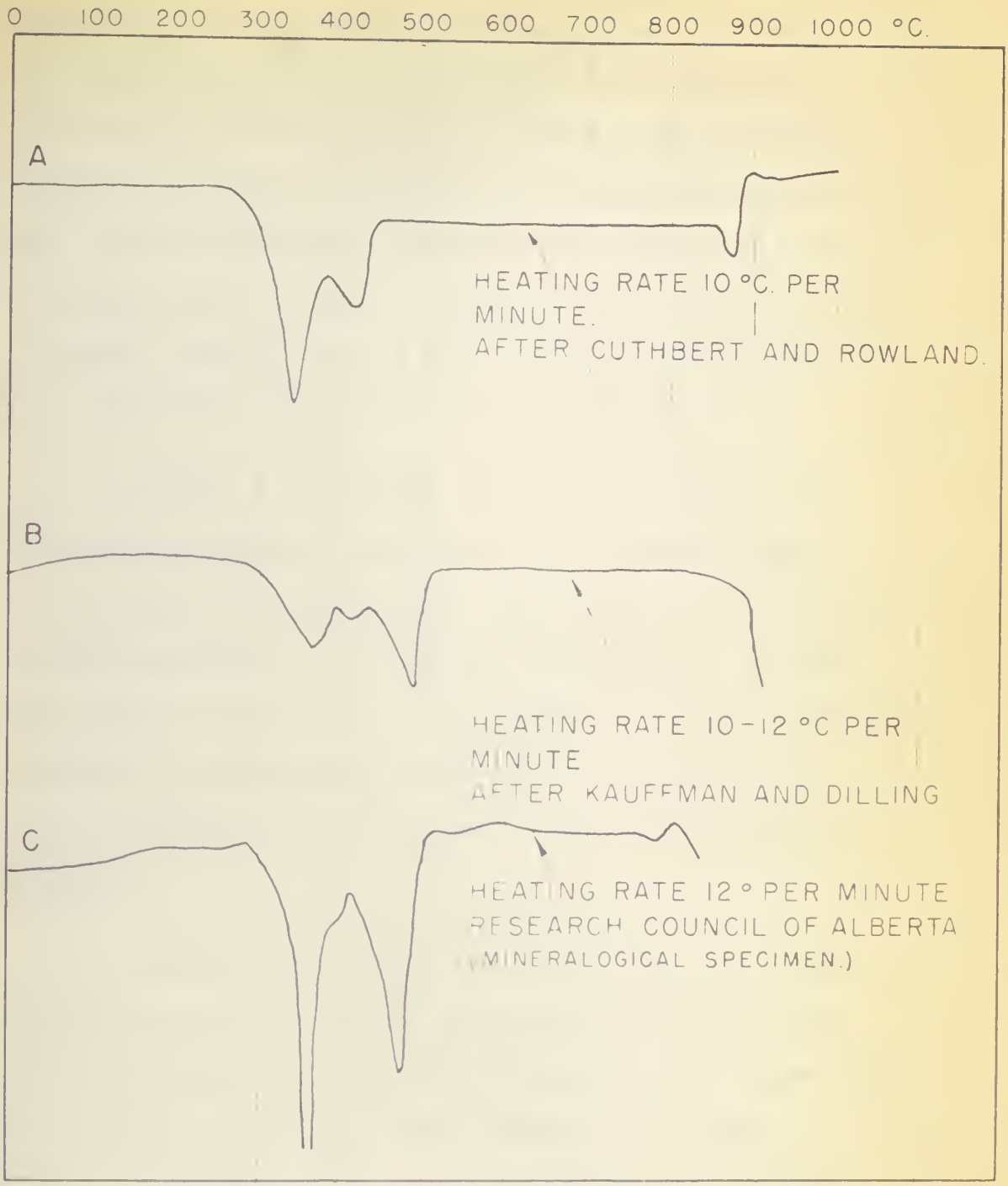


FIGURE 11. THERMAL CURVES OF CERRUSITE AT FAST HEATING RATES.

collection at the University of Alberta was first crushed and then hand-picked under the microscope to remove impurities. The material so obtained consisted of about 10 gms. of opaque clusters of prismatic cerrusite crystals. These were ground to pass a 200 mesh screen and then mixed with a diluent of chemically pure Al_2O_3 powder of -200 mesh particle size in the ratio of 4:1 by weight. Thermal curves of the diluted cerrusite (Appendix 7) were then obtained using various rates of heating.

Curve C - 1. Heating rate of 12°C per minute. The curve shows a progressive exothermic shift below 200°C due to fluctuations in the heating rate. Two endothermic reactions are recorded beginning at 290°C and 410°C respectively. The first peak shows an interference at about 385°C which may be an expression of another reaction taking place concurrently with the first and which corresponds to the middle peak obtained by Kauffman and Dilling.

Curve C - 2. Heating rate of 6°C per minute. Three distinct endothermic reactions are recorded between 280°C and 470°C. The middle reaction is superimposed on the ones preceeding and following, and is represented only by a small peak.

Curve C - 3. Heating rate, 4°C per minute. Again three distinct endothermic reactions are recorded between 380°C and 470°C. The peaks are well defined and the middle one, although still superimposed, reaches a maximum amplitude.

Curve C - 4. Heating rate, 2.5°C per minute. The reactions are now reflected by broader peaks, but still distinct. The initial dissociation temperature remains approximately at 280°C but the temperature at which the dissociation is completed is lowered to 420°C.

Curve C - 5. (Not shown in the Appendix) Heating rate, 1°C per minute. The peaks reflecting the three reactions are now reduced to broad loops, with the resultant difficulty in determining the temperatures at which the dissociation starts and ends.

The d.t.a. curves for the dissociation of cerrusite when this mineral is heated at less than 6°C per minute indicate three endothermic reactions between 290°C and 430°C. This agrees with the chemical data. At faster heating rates these endothermic reactions are not revealed by the d.t.a. apparatus because the peak corresponding to the second reaction is obscured by those preceeding and following it. This suggests that heating rate is an important parameter in a differential thermal investigation and that the shape of all thermal curves should be regarded as good only for one particular rate of heating.

Measurement of the peak areas for the total endothermic deflections of the three curves indicate that the total endothermic effect was approximately the same for each dissociation:

Curve C - 1	-	65	sq.cms. (estimated)
Curve C - 2	-	65	sq.cms. (measured)
Curve C - 3	-	68	sq.cms. "
Curve C - 4	-	65	sq.cms. "
Curve C - 5	-	66.5	sq.cms. "

D. Previous Studies on the d.t.a. of Magnesite.

The difference in the form of several published thermal curves for the dissociation of magnesite is very marked. Faust (7) obtained the thermal curve of a "pure" magnesite which showed a small exothermic peak following the main endothermic peak. Beck (2) obtained a curve showing a single endothermic peak between 500°C and 700°C and which had a definite interference near 600°C on the initial slope of the peak. X-ray studies to determine whether this change in slope was due to the formation of an oxy-carbonate were inconclusive.

Kulp et al. (14) published 10 thermal curves of different magnesite specimens, some of which show a single endothermic peak between 500°C and 750°C while others show this peak immediately followed by a small exothermic peak and a smaller endothermic one. They consider t e single large endothermic peak to be characteristic of the mineral and relate the smaller peaks to the oxidation of FeO to Fe_2O_3 and the decomposition of small amounts of calcite.

E. Experimental Procedure and Discussion of Results.

A single mineralogical specimen of rhombohedral magnesite was crushed and hand-picked under the miscroscope in order to remove impurities. The material was ground to minus 200 mesh particle size and mixed with pure Al_2O_3 powder of the same particle size in varying proportions by weight. Thermal curves of the diluted magnesite (Appendix 8) were then obtained using various heating

rates and, in some cases, after the specimen had been leached in distilled water.

Curve M - 1. Heating rate of 10°C per minute. Dilution, 25% by weight Al_2O_3. Dissociation began at 420°C and ended abruptly at 700°C. This resulted in an endothermic peak which was not contained on the chart although the thermocouple potentiometer circuit was adjusted to give a base-line on the extreme left-hand side of the chart. Estimated amplitude of peak, 25 cms., estimated area, 68 sq.cms. A smaller endothermic reaction occurs between 750°C and 860°C and correlates with that obtained by Kulp.

Curve M - 2. Heating rate of 8°C per minute. Dilution, 35% by weight Al_2O_3. The major endothermic dissociation now begins at about 375°C and ends at 725°C. Estimated amplitude of peak, 22 cms., estimated area 71 sq.cms. The smaller endothermic reaction between 750°C and 860°C is still present.

Curve M - 3. Heating rate of 6°C per minute. Dilution, 40% by weight Al_2O_3. The major endothermic reaction begins at about 450°C and ends at 670°C. An interruption in the peak occurs at 555°C. The measured amplitude is 14.7 cms., the measured area is 66.5 sq.cms. The second smaller endothermic peak occurs at the same temperatures as in the previous curves but is broken by an interruption at 820°C. Four other specimens run under the same conditions produced the same curve.

Curve M - 4. Heating rate of 4°C per minute. Dilution,

40% by weight Al_2O_3. This specimen was leached in distilled water for 3 hours and then dried at 90°C before heating. A smooth base-line is established and the major endothermic deflection begins very gradually at 400°C and ends at 680°C. No interruption in the initial slope of the peak is recorded. The measured peak amplitude is 8.3 cms., the measured area is 34 sq.cms. The second endothermic reaction takes the form of a low loop between 750°C and 830°C.

None of these curves shows precise evidence for intermediate stages in the thermal dissociation of magnesite. At a heating rate of 6°C per minute and with 40% by weight Al_2O_3 dilution (Curve M - 3) , a change in slope of the endothermic peak is recorded at 555°C. In relation to the total endothermic heat effect, this interruption corresponds to that shown in the curve obtained by Beck (2), but unfortunately he does not specify the rate of heating.

The smaller endothermic effects recorded on all the curves between 750°C and 860°C are probably due to the dissociation of small quantities of calcite, but the interrupted shape of the one obtained in curve M - 3 suggests the presence of dolomite as well.

Varying amounts of dilution do not permit comparison of the total endothermic effects.

VII. SUMMARY

While the effects of various techniques in the preparation of carbonate minerals for differential thermal analysis have received wide attention, those caused by variation in heating rate have been neglected. It is apparent from this study that in the d.t.a. of cerrusite and magnesite, heating rate is an important factor. The maximum information on the dissociation of these minerals is obtained when heating rates of between 3°C and 6°C per minute are used. For the analysis of dolomitic limestones, a heating rate of 6°C per minute also gives a characteristic curve which is experimentally reproducible and therefore permits comparative measurement of peak areas.

In the d.t.a. of dolomitic limestones and synthetic calcite-dolomite mixtures, the peak area corresponding to the first stage in the dolomite dissociation has been found to be proportional to the dolomite concentration. However, curves plotting percent dolomite against peak area for two series of dolomitic limestone samples differ from that obtained for the synthetic mixtures. These two curves indicate an excess of MgO in the dolomitic limestone that is not in the form of dolomite.

A heating rate of 4°C per minute has been found to give a thermal curve for cerrusite which indicates the formation of a series of oxy-carbonates between 380°C and 470°C. This agrees with the published chemical data.

Thermal curves for magnesite, obtained at heating rates varying between 4°C and 10°C, do not show evidence for the formation of an oxy-carbonate series which has been reported in the chemical literature.

Variations in the specimen weight of a calcite-dolomite sample between 0.35 gms and 0.23 gms. did not effect the area of the lower-temperature dolomite peak. Specimens weighing less than 0.23 gms recorded a proportional decrease in peak area. This indicates that there is an upper limit to the weight of specimen that can contribute to the differential thermal record, providing that the degree of packing remains constant.

REFERENCES

1. MARSHAL, I., Temperature and heat of reaction calibration of the differential thermal analysis apparatus; Am. Mineral., 37, pp. 667-694, (1952).

2. BECK, C.W., Differential thermal analysis curves of carbonate minerals; Am. Mineral., 35, pp. 985-1013, (1950).

3. BERG, L.G., Influences of salt admixtures upon dissociation of dolomite; Compt. Rend. (Doklady) Acad. Sci. U.S.S.R., 38, pp. 24-27, (1943).

4. BERG, L.G., Area measurement in thermograms for quantitative estimates and determinations of heats of reaction; Compt. Rend. Acad. Sci. U.S.S.R., 49, pp. 668-671, (1945).

5. BROWN INSTRUMENT CO., Brown Electronik strip chart recorder operating instructions; Instruction Manual 1563BG.

6. CUTHBERT, F.L., and McLAUGHLIN, R.P.D., Differential thermal analysis of some carbonate minerals: Am. Mineral., 32, pp. 111-115, (1947).

7. FAHEY, J.J., Dedolomitization, and its relation to a possible derivation of a magnesium rich hydrothermal solution; Am. Mineral., 34, pp. 799-803, (1949).

8. GRIM, R.E., Preliminary report on the variations in differential thermal curves of low-iron dolomites, Am. Mineral., 37, pp. 1-27, (1952).

9. HASE, H.A.T., and [illegible], L., Differential thermal analysis of the dolomite composition, Am. Mineral., 37, pp. 165-179, (1952).

10. INTERNATIONAL CRITICAL TABLES, 7, p. 250, First Edition, (1930).

11. KAUFFMAN, H.A., and [illegible] ILLING, H.V., Differential thermal curves of certain minerals: Econ. Geol. 45, pp. 292-296, (1950).

12. KERR, P.F., and HUNT, J.M., Multiple thermal analysis; Science, 106, No. 2729, (1947).

13. KERR, P.F., KULP, J.L., and HAMILTON, P.K., Differential thermal analysis of reference clay mineral specimens; A.P.I. Project 49, Preliminary Report 3, (1949).

14. KULP, J.L., KENT, P., and KERR, P.F., Thermal study of the Ca-Mg-Fe carbonate minerals, Am. Mineral., 36, pp. 643-670, (1951).

15. ROWLAND R.A., and BECK, C.W., Determination of small quantities of dolomite by differential thermal analysis, Am. Mineral., 37, pp. 76-82, (1952).

16. ROWLAND R.A., and LEWIS, D.R., Furnace atmosphere control in differential thermal analysis; Am. Mineral., 36, pp. 80-91, (1951).

17. ROGINSKI and SHULTZ. Chem. Abs., 15, p. 618, (1928).

18. SERSALE, R., Chem. Abs., 45, p. 7921, (1951).

19. TZENTNERSHVER, M., and BRUCS, R., Chem. Abs., 19, p. 2159, (1925).

20. TZENTNERSHVER, M., FALK, G., and ADERBACH, A., Chem. Abs., 19, p. 1363, (1925).

21. WILSDORF, H.G.F., and HALL, E.A.N., X-ray study of the thermal decomposition of dolomite; Nature, 167, pp. 945-946, (1951).

22. WITTELS, M., Some aspects of mineral colorimetry; Am. Mineral., 36, pp. 760-767, (1951).

APPENDIX 9

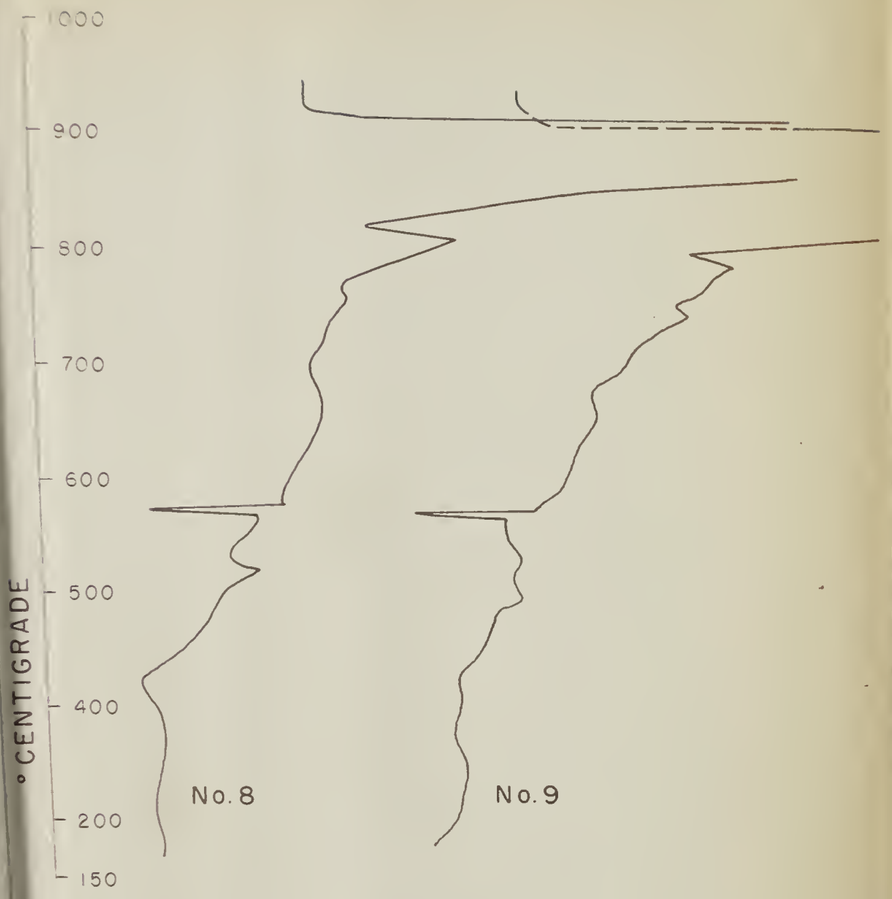
In the d.t.a. of the calcite-dolomite specimens, fused silica glass was used as a diluent. This choice of diluent may be questioned on the basis of possible reactions between both the Ca and Mg carbonates and the SiO_2. Comparison of curves obtained from two specimens of a particular calcite-dolomite sample, diluted respectively with silica and alundum, shows identical lower-temperature peaks. This suggests that no magnesium silicates were formed during analysis of the first specimen and that the percentage dolomite relationship to the lower-temperature peak area remains valid.

The higher-temperature peak for the silica-diluted specimen indicated a small reduction in the amount of $CaCO_3$ available for dissociation at that temperature. This could result from the formation of wollastonite,

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2,$$

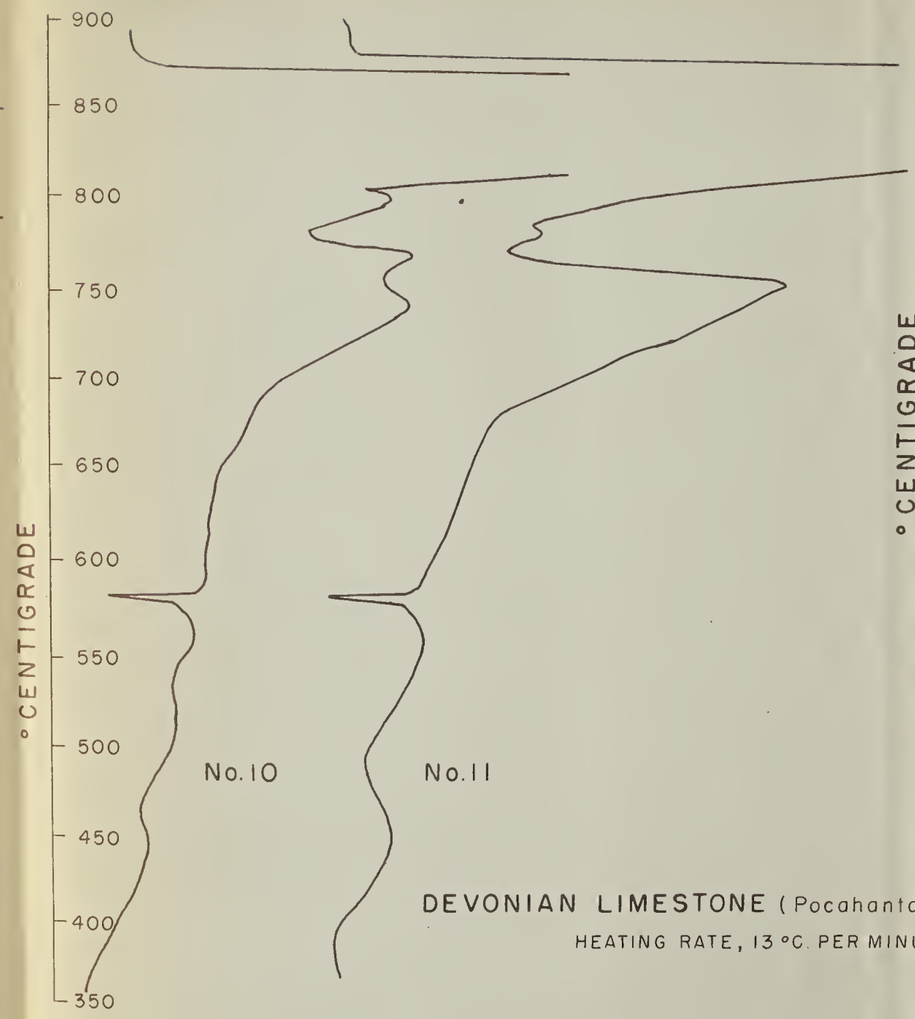
which according to Danielson, see Mason (23), may take place above 280°C and under a pressure of one atmosphere of CO_2.

The problem here encountered is a fundamental one and emphasizes the usefulness of thermal analysis as a new approach to the study of metamorphism. In the d.t.a. of siliceous dolomites, the reactions between the carbonates and silica to form forsterite (Mg_2SiO_4), diopside ($CaMgSi_2O_6$) etc. may become apparent only when extremely slow heating rates are used, and when control of atmosphere composition and pressure are effected. These silicate reactions may be further studied by removing the products of thermal analysis at different temperatures and by examining them by x-ray, optical and chemical methods.



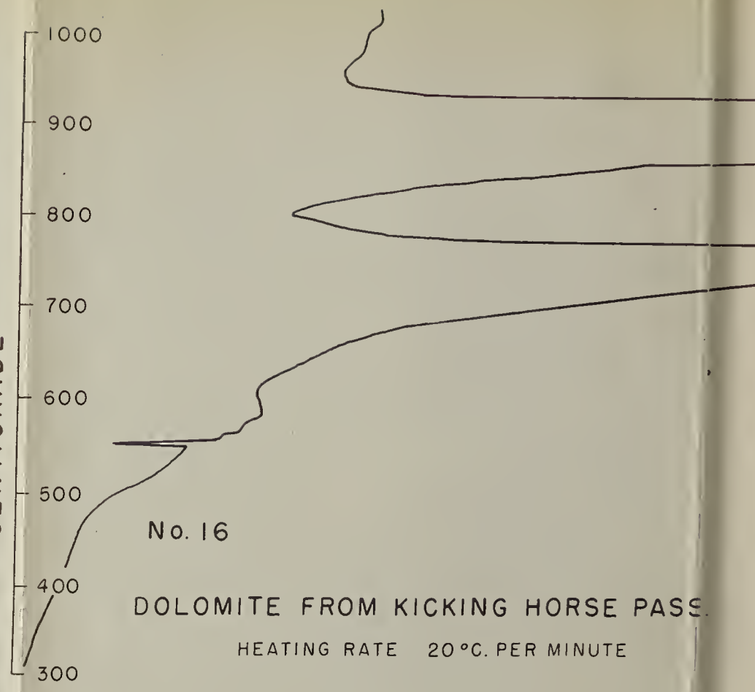
DEVONIAN LIMESTONE (Pocahantas Quarry)

HEATING RATE, 16°C. PER MINUTE



DEVONIAN LIMESTONE (Pocahantas Quarry)

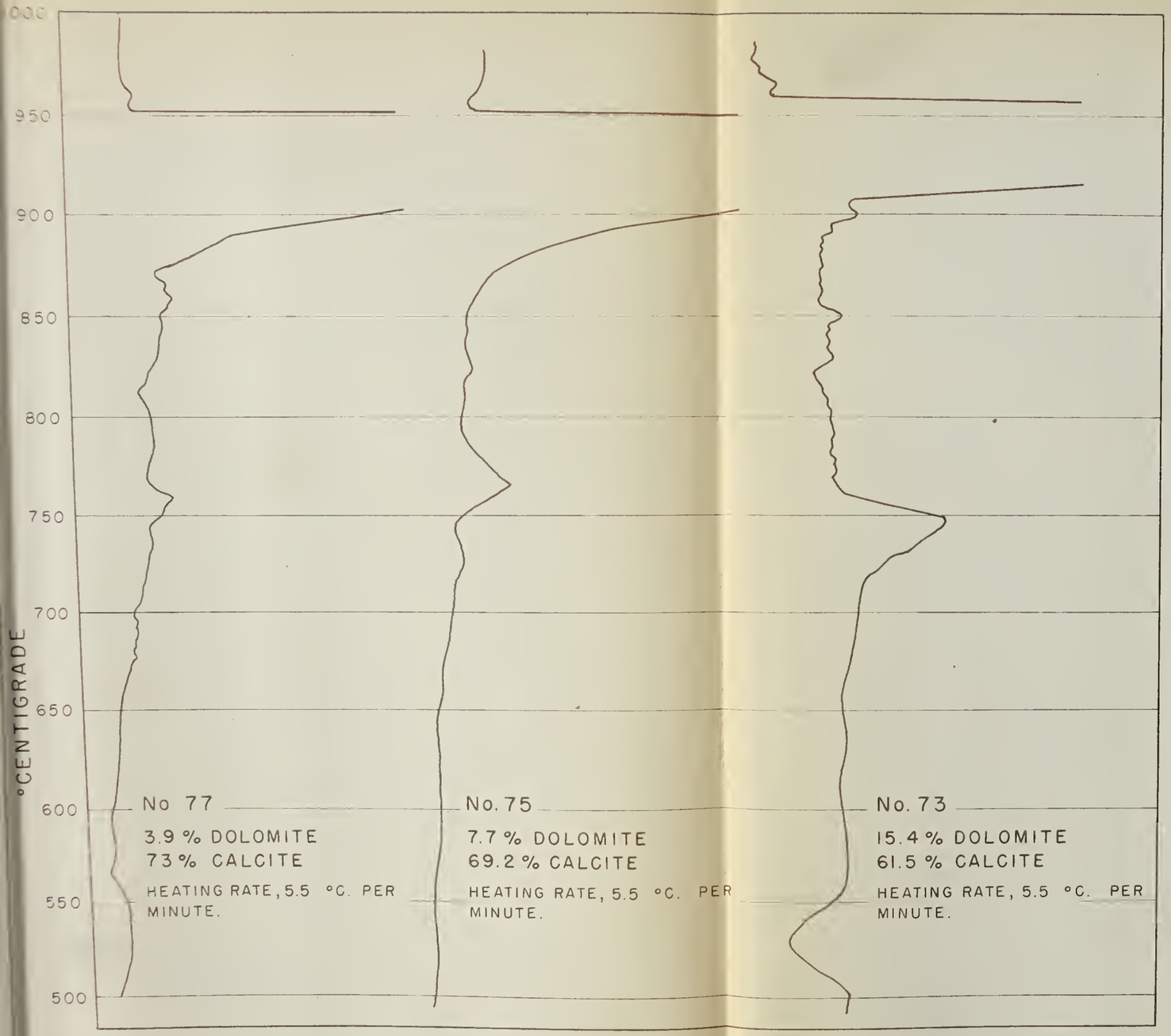
HEATING RATE, 13°C. PER MINUTE

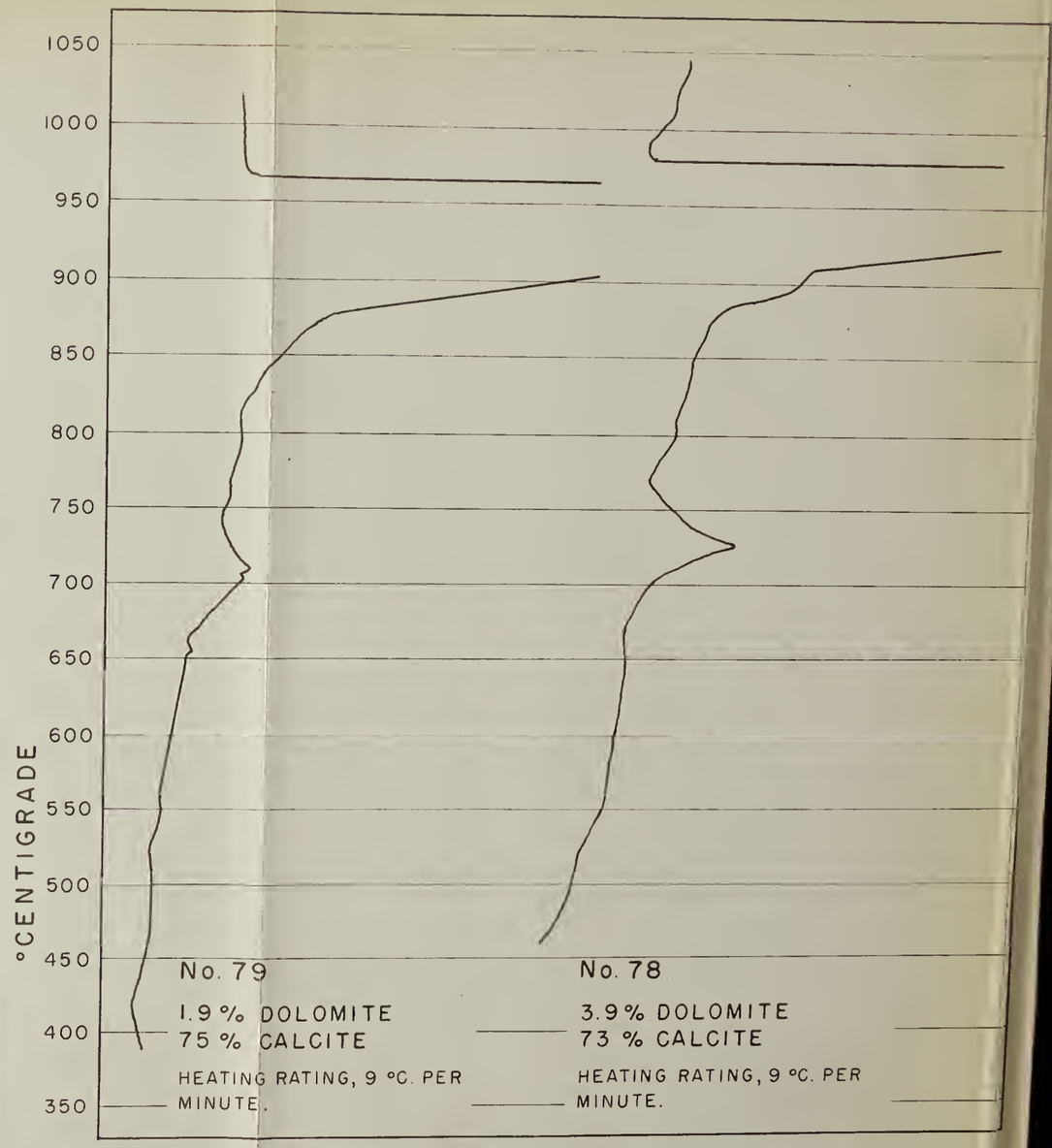


DOLOMITE FROM KICKING HORSE PASS.

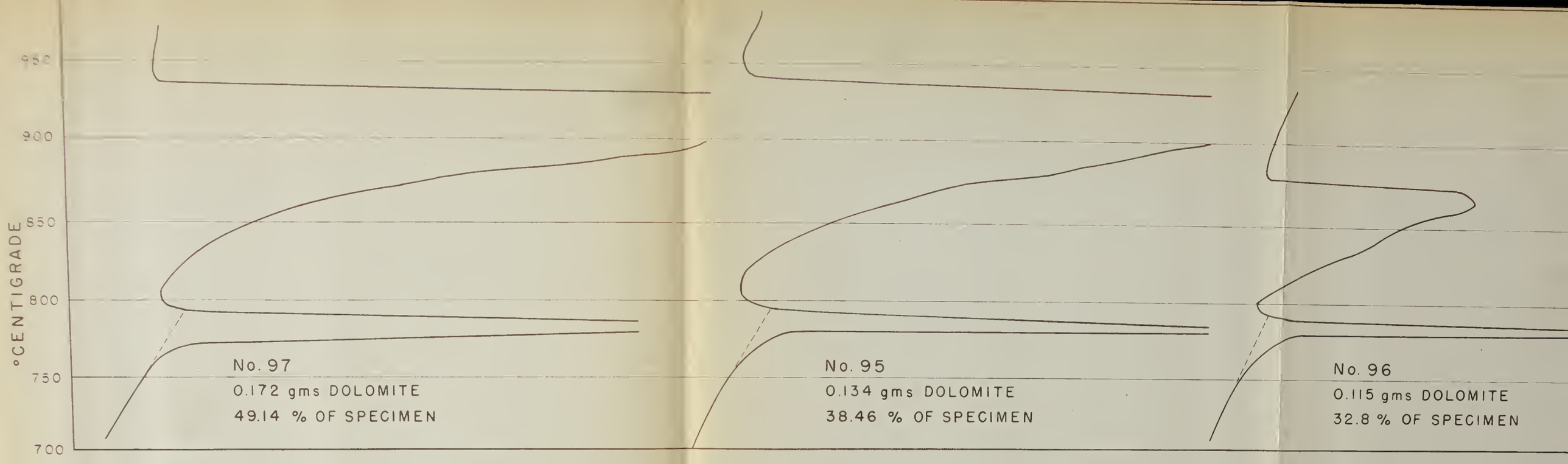
HEATING RATE 20°C. PER MINUTE

APPENDIX 2. PRELIMINARY THERMAL CURVES.

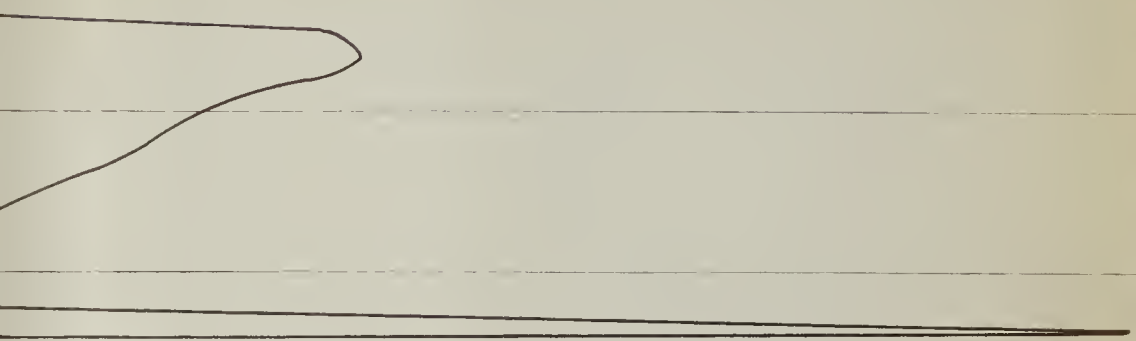




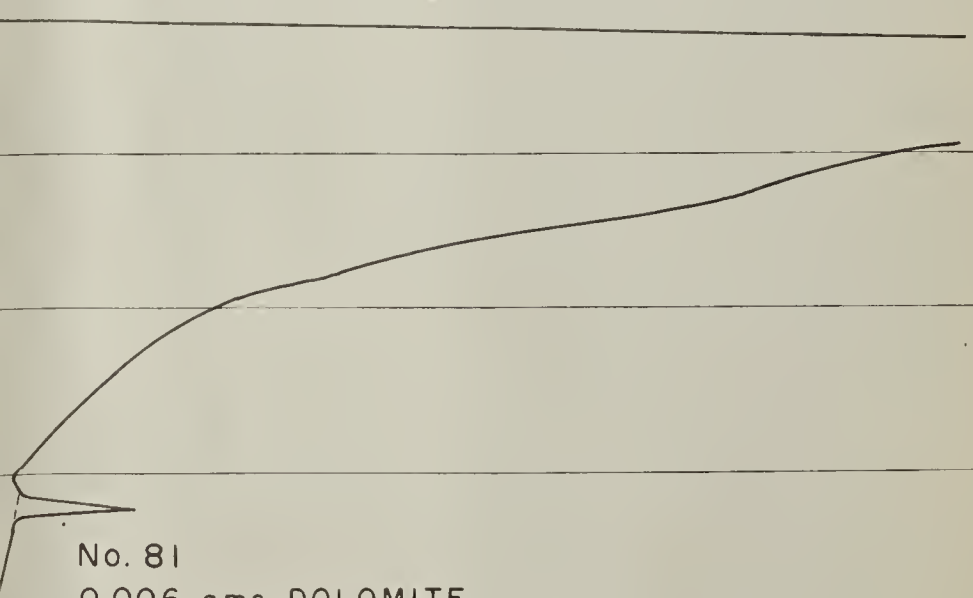
APPENDIX 3. PRELIMINARY THERMAL CURVES OF DOLOMITE / CALCITE MIXTURES HEATED IN A CO_2 ATMOSPHERE.



APPENDIX 4. THERMAL CUR
DOLOMITE / C

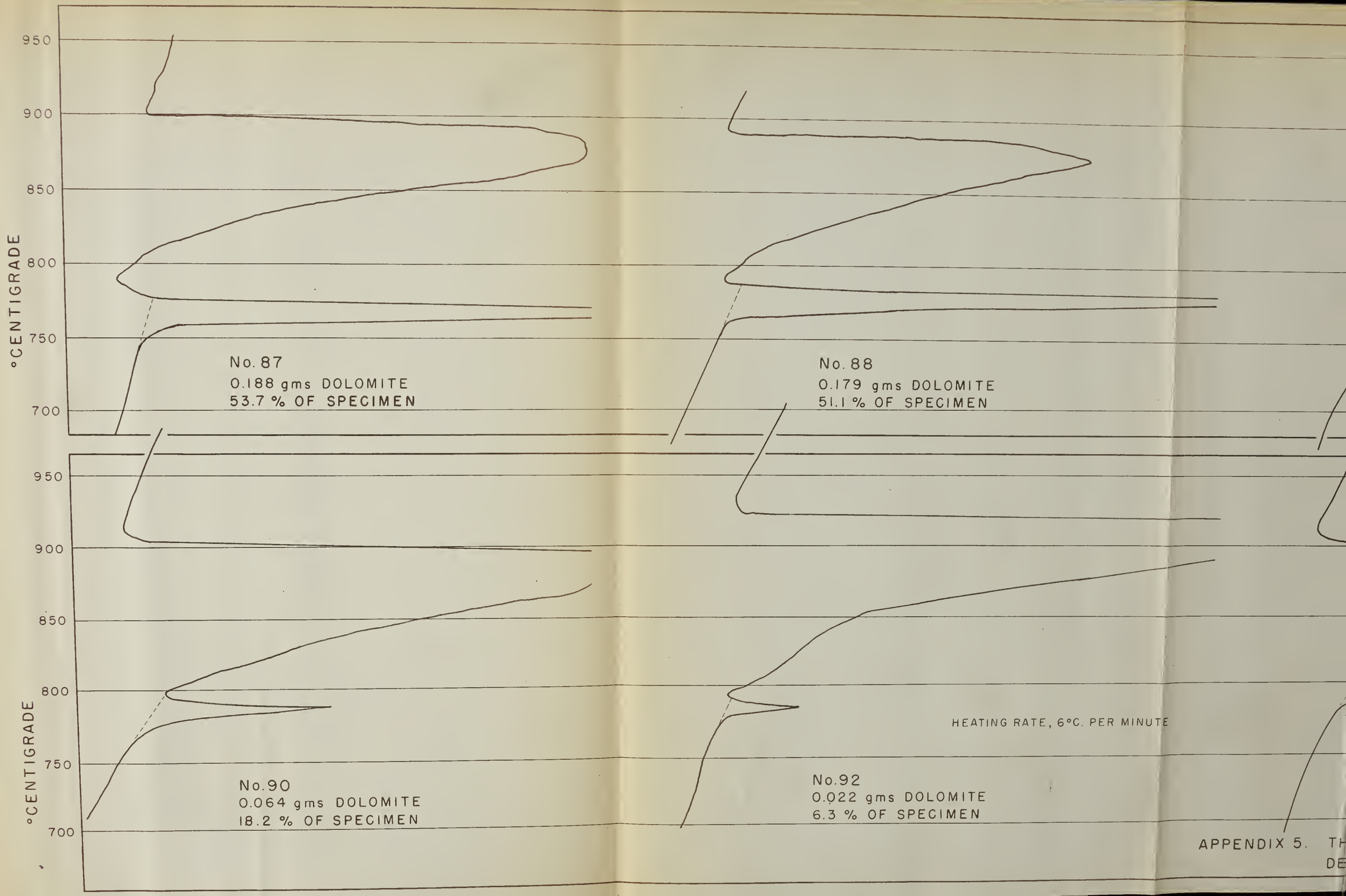


No. 96
0.115 gms DOLOMITE
32.8 % OF SPECIMEN

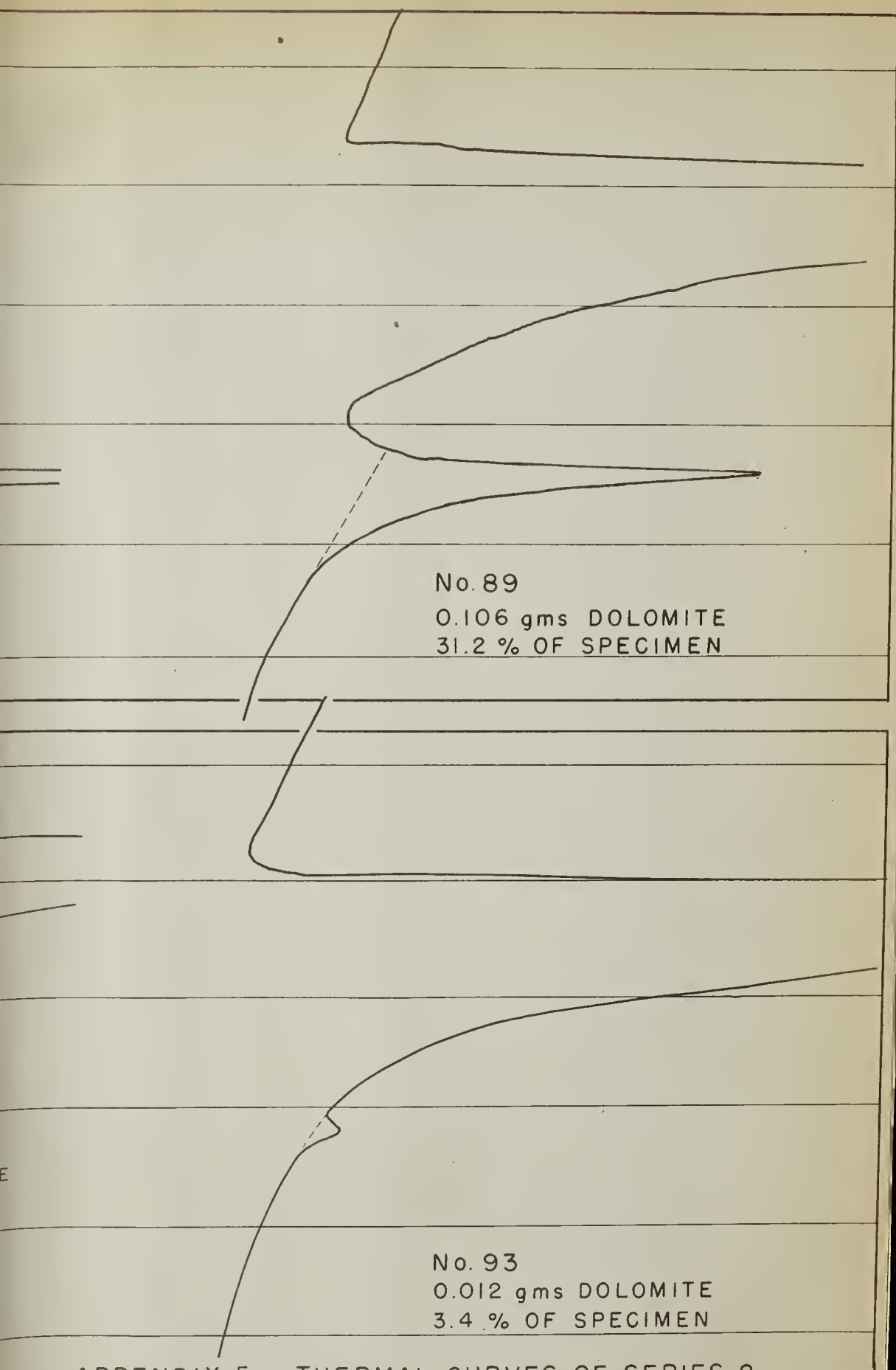


No. 81
0.006 gms DOLOMITE
1.92 % OF SPECIMEN

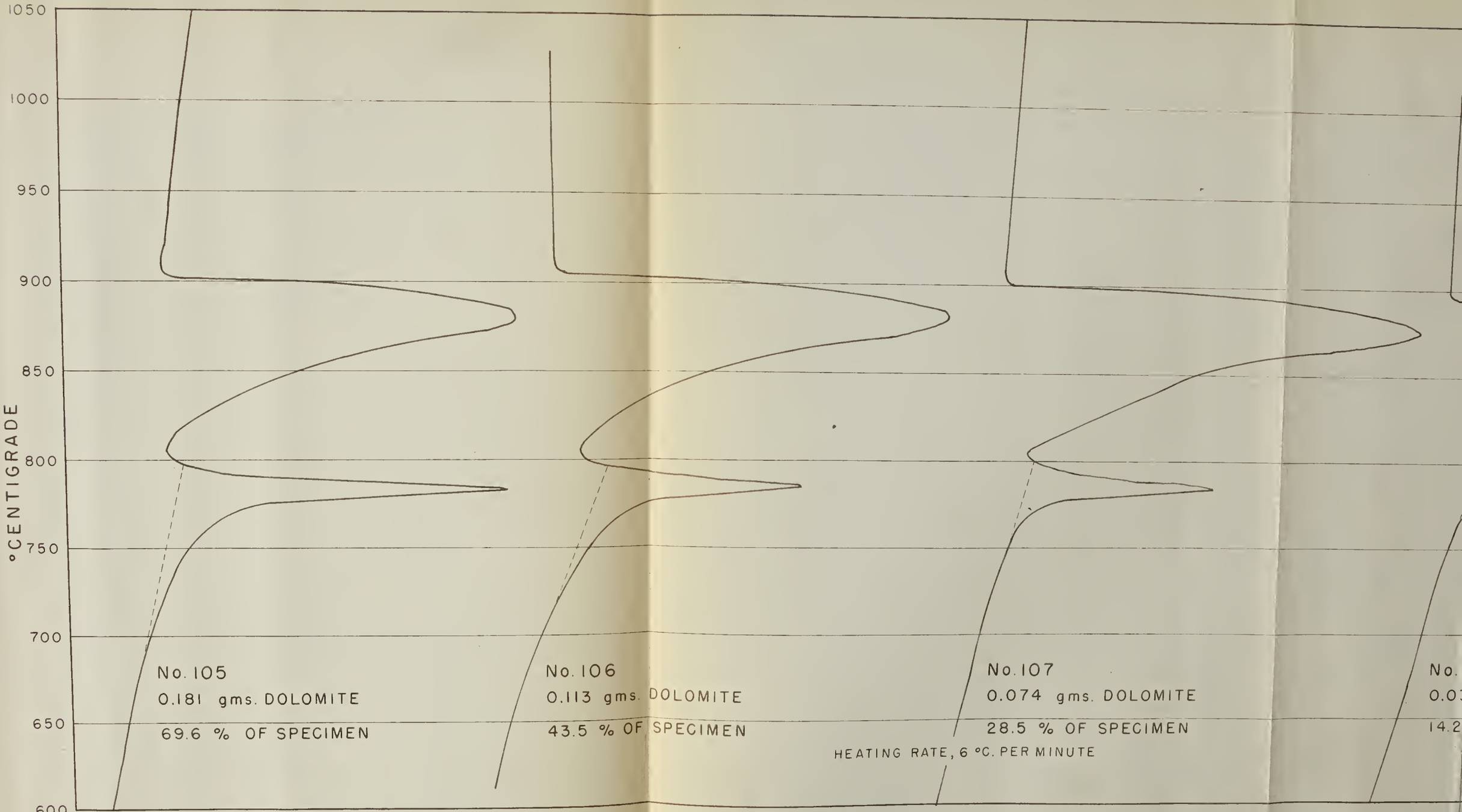
APPENDIX 4. THERMAL CURVES OF SERIES I,
DOLOMITE / CALCITE MIXTURES.



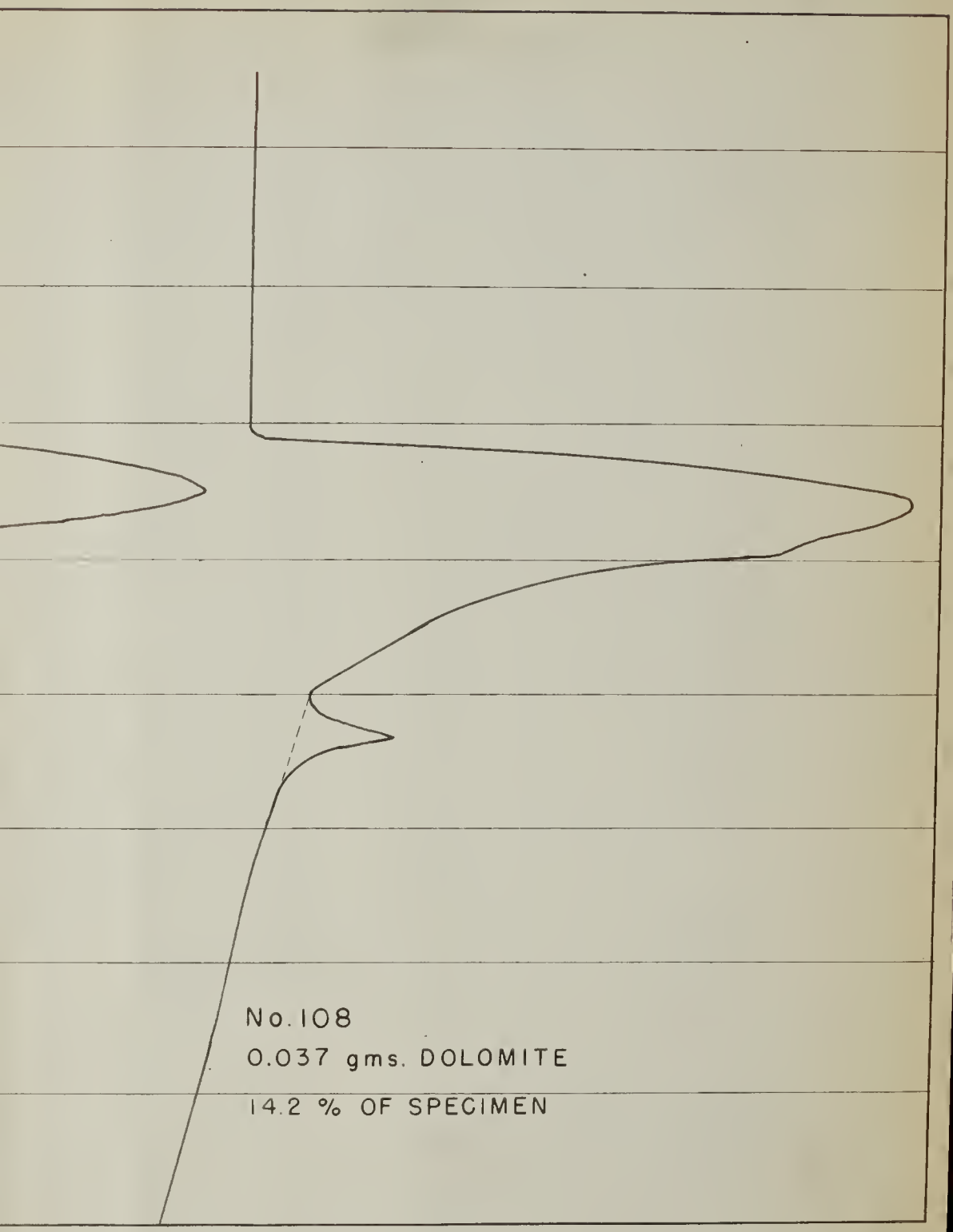
APPENDIX 5. TH
DE



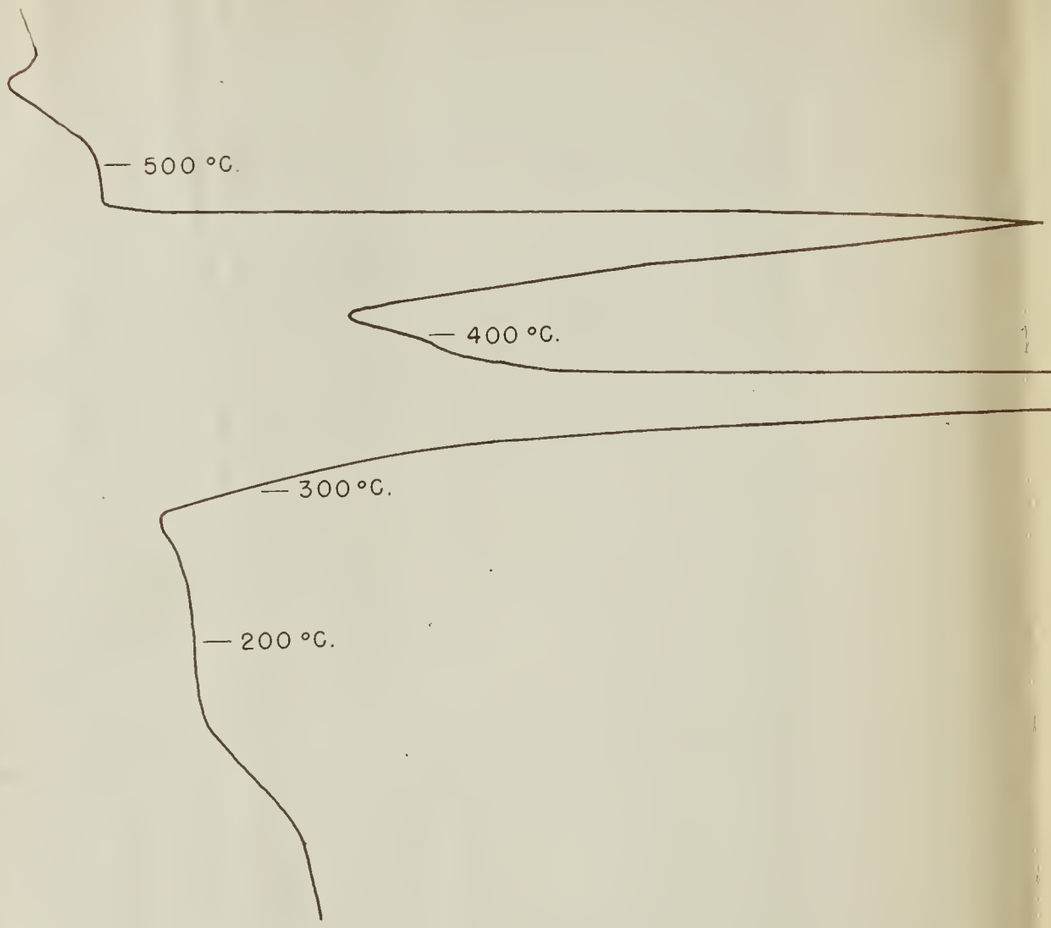
APPENDIX 5. THERMAL CURVES OF SERIES 2, DEVONIAN DOLOMITIC LIMESTONE


1050
1000
950
900
850
800
750
700
650
600
°CENTIGRADE
No. 105
0.181 gms. DOLOMITE
69.6 % OF SPECIMEN
No. 106
0.113 gms. DOLOMITE
43.5 % OF SPECIMEN
No. 107
0.074 gms. DOLOMITE
28.5 % OF SPECIMEN
HEATING RATE, 6 °C. PER MINUTE

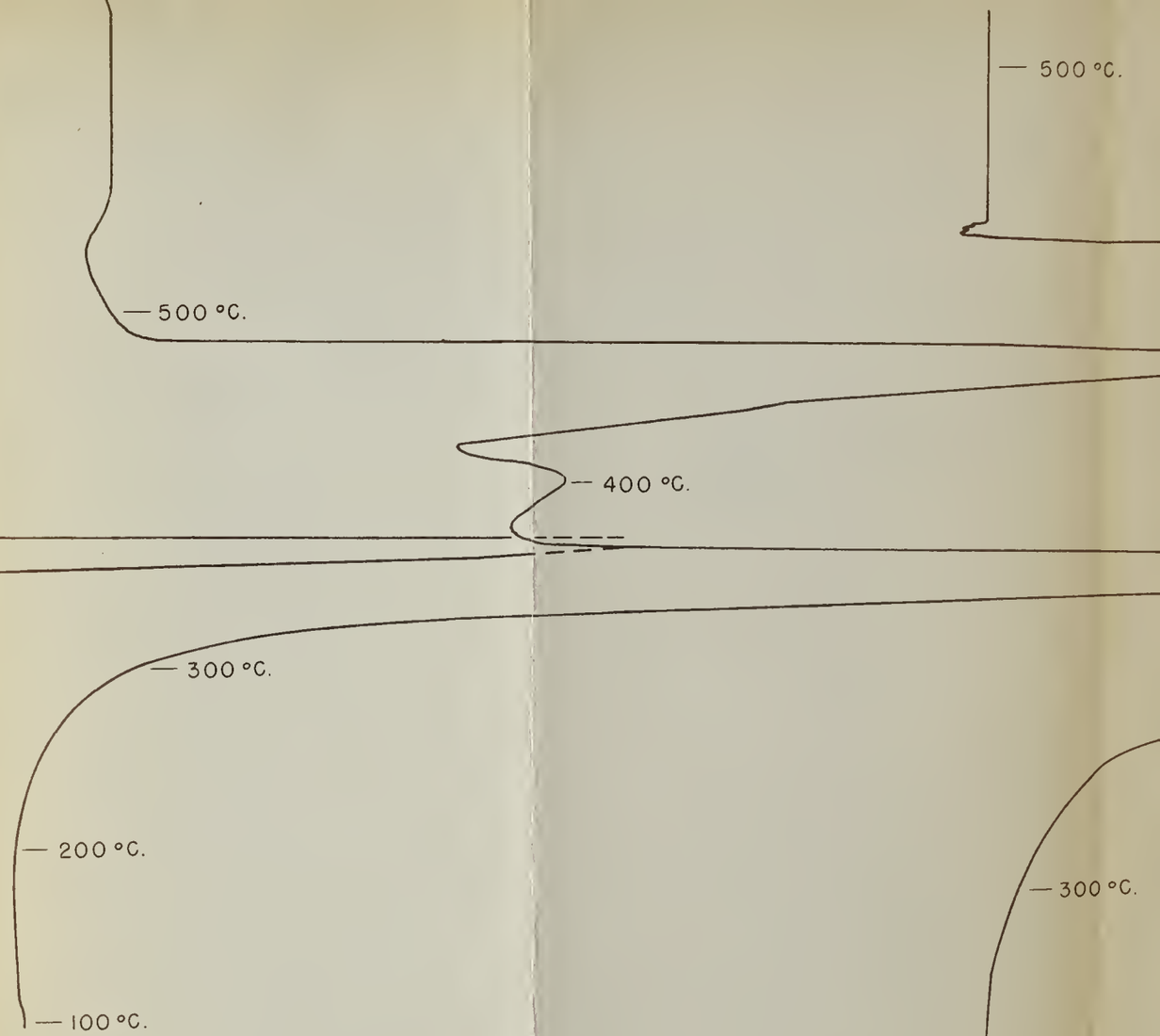
APPENDIX 6



APPENDIX 6 THERMAL CURVES OF SERIES 3.
STANDARD DOLOMITIC LIMESTONE

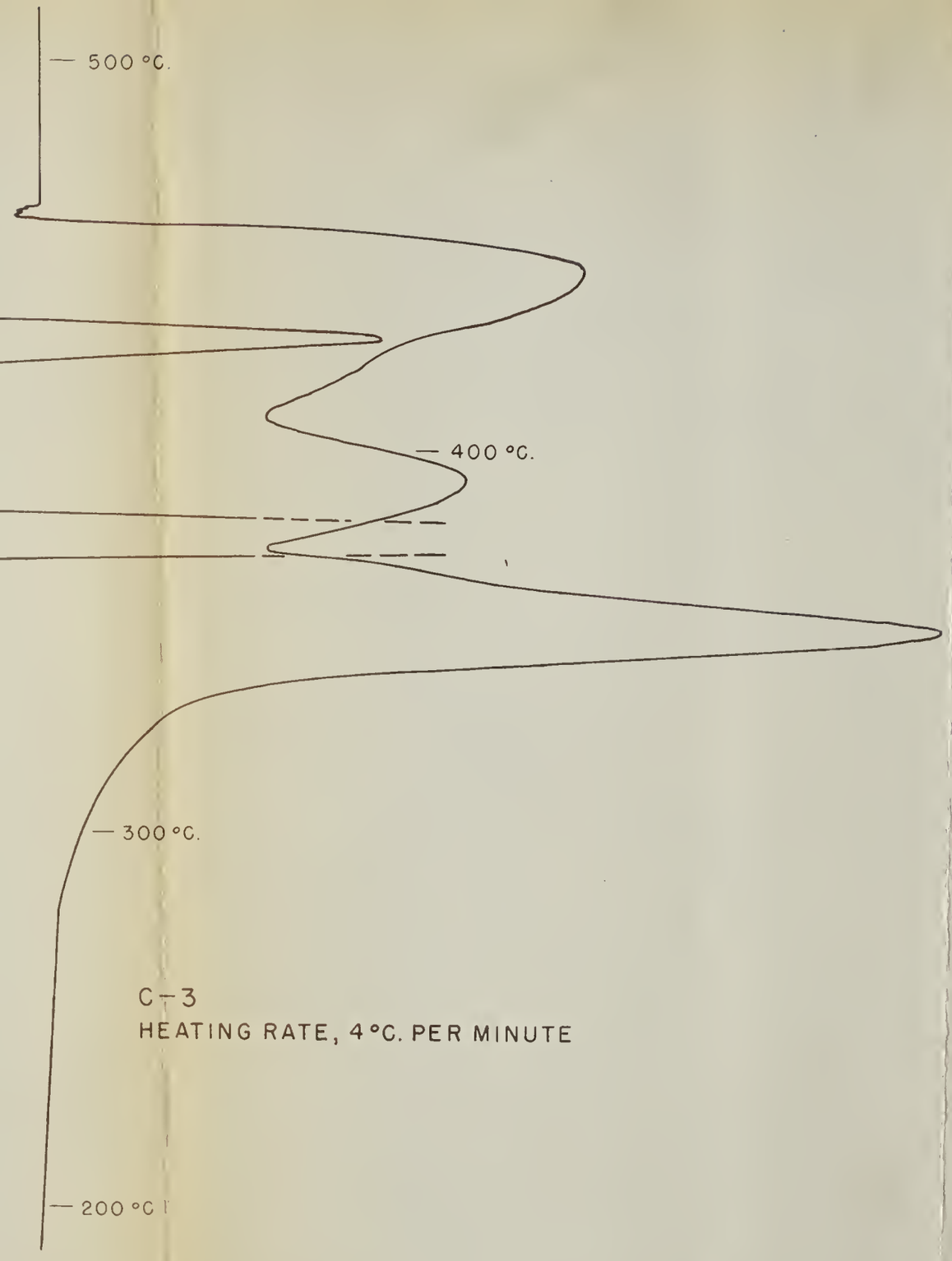


C-1
HEATING RATE, 12 °C. PER MINUTE

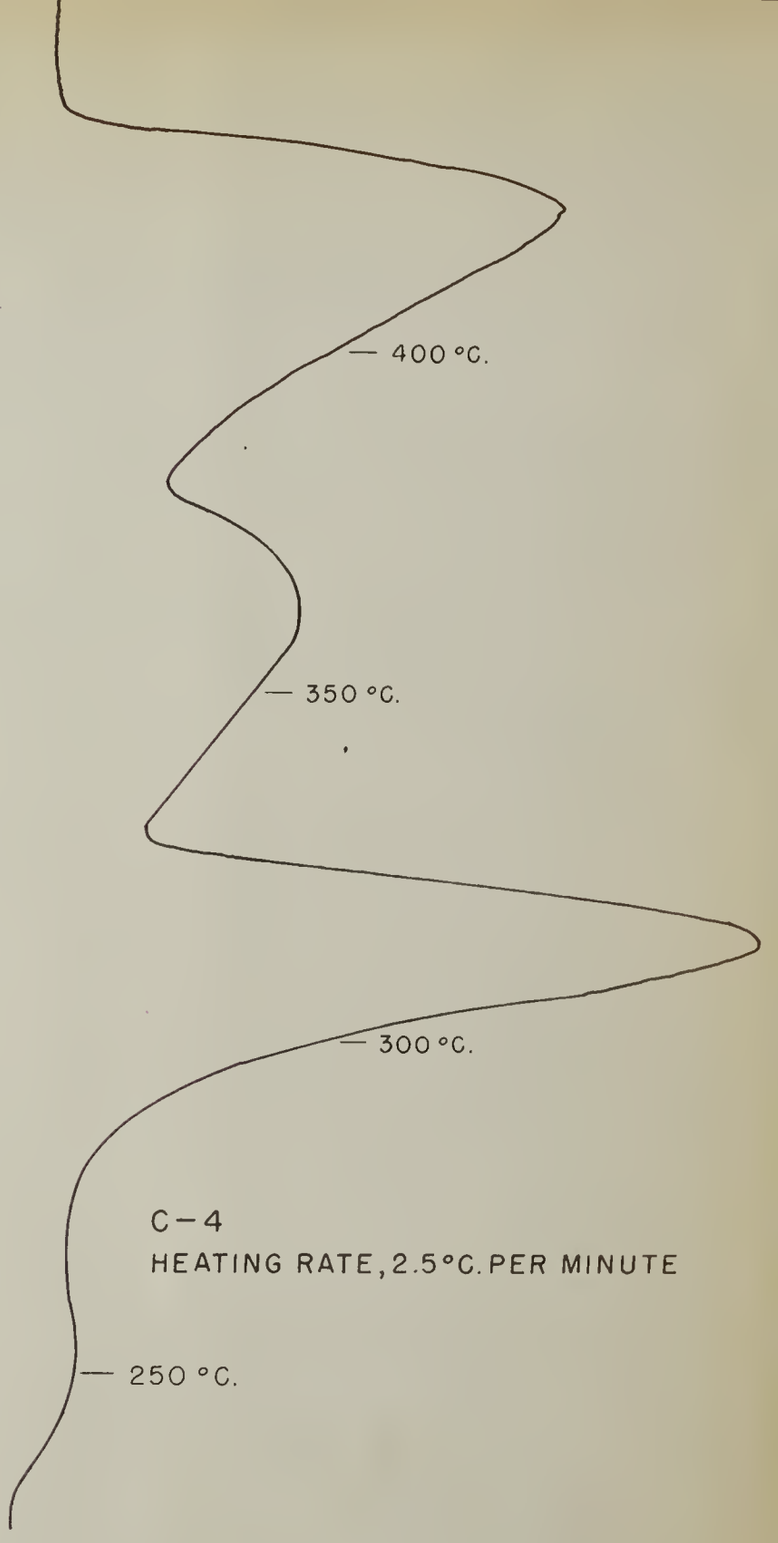


C-2
HEATING RATE, 6°C. PER MINUTE

C-3
HEATIN

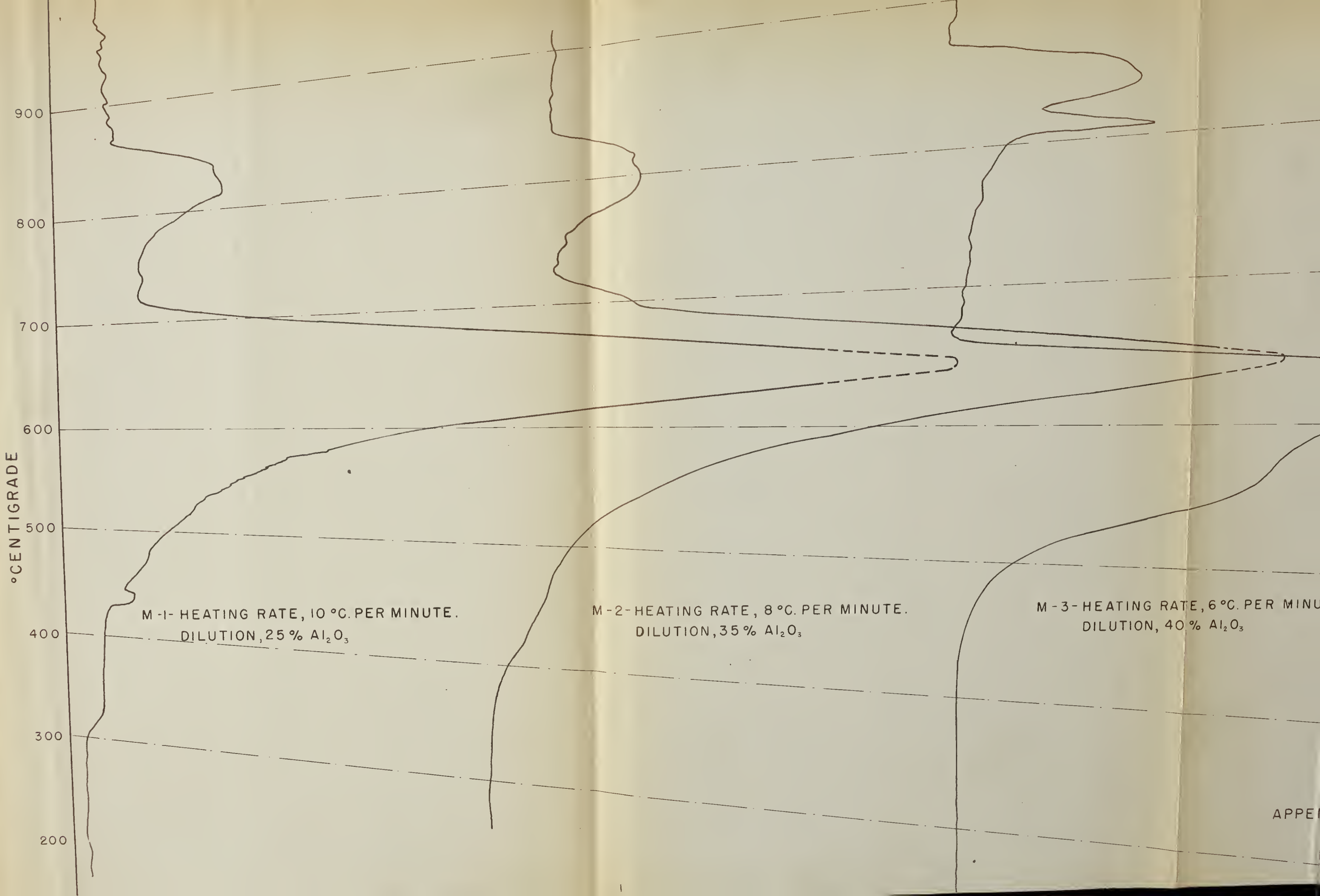


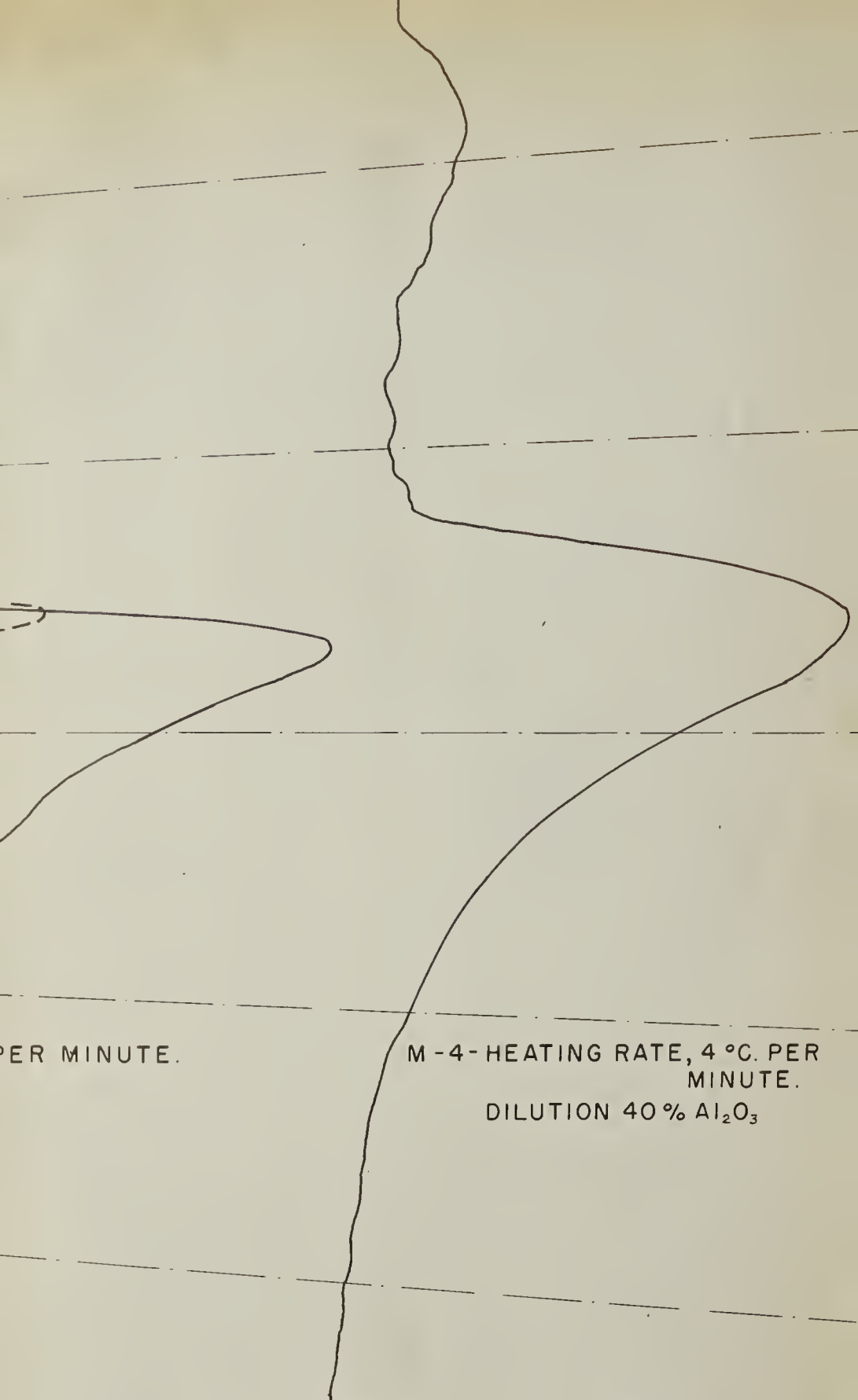
C—3
HEATING RATE, 4 °C. PER MINUTE



C—4
HEATING RATE, 2.5 °C. PER MINUTE

APPENDIX 7. THERMAL CURVES OF CERRUSITE.


900
800
700
600
500
400
300
200
°CENTIGRADE
M-1- HEATING RATE, 10 °C. PER MINUTE.
DILUTION, 25 % Al_2O_3
M-2-HEATING RATE, 8 °C. PER MINUTE.
DILUTION, 35 % Al_2O_3
M-3-HEATING RATE, 6 °C. PER MINU
DILUTION, 40 % Al_2O_3
APPE



APPENDIX 8 THERMAL CURVES OF MAGNESITE

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